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#### Mass Transport in Gas-evolving Electrolysers

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#### MASS TRANSPORT IN GAS-EVOLVING ELECTROLYZERS

#### MASS TRANSPORT IN GAS-EVOLVING ELECTROLYZERS

#### Dissertation

for the purpose of obtaining the degree of doctor at Delft University of Technology by the authority of the Rector Magnificus Prof. dr. ir. T.H.J.J. van der Hagen Chair of the Board for Doctorates to be defended publicly on Tuesday 15 April 2025 at 15:00 o'clock

by

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## **SUMMARY**

In 2023, renewable energy generation reached an all-time high, with 29% of all electricity coming from renewable sources. However, electrical energy will not be able to fully replace fossil fuels, as the intermittency of renewable sources requires additional solutions to match the energy demand. Additionally, conversion to chemical bonds is required to supply chemicals for plastics, fertilizers, steel, etc. Electrolysis – particularly water and  $CO_2$  electrolysis – offer a promising solution to these problems by converting renewable electricity into fuels and chemical building blocks. Although electrolysis processes are very promising for the energy transition, their costs are currently still too high.

This thesis focusses on the role that gas bubbles have on the performance of electrolysers: the formation of gas bubbles is inevitable in most electrolysers, since the common electrolysis products (e.g.  $H_2$ ,  $O_2$  or CO) have a poor solubility in water. Controlling the behaviour of gas bubbles offers a pathway to lower the cell voltage or improve the mass transport, which allows operation at higher operating current densities. This could help with decreasing the costs of electrolysers, bringing them closer to competing with fossil fuel-based processes.

Gas bubbles increase the cell voltage of electrolysers, as they reduce electrolyte conductivity and block a section of the active electrode surface area. To mitigate these effects, we introduce a zero-gap alkaline water electrolyser that operates with a periodic pressure swing to remove the gas bubbles (Chapter 2). The pressure swing creates a state of the electrolyser with and without gas bubbles, which allows us to measure the effects of gas bubbles on cell voltage *in situ*. The electrode geometry and electrolyte conductivity are the main factors that dictate voltage losses due to gas bubbles, while effects of operating pressures between 2-5 bar had a limited influence on the volltage losses by bubbles. A pressure swing also allows us to reduce the time-averaged cell voltage. We manage to reduce the irreversible energy losses (i.e. resulting from overpotentials) by 5% when using 1 M KOH, 30 °C and nickel foam electrolyte conductivity (80 °C, 30% KOH) results in very small bubble voltage losses, making a pressure swing only marginally effective.

Despite their drawbacks, gas bubbles can also benefit electrolysers. The growth, coalescence, and movement of bubbles contribute to the mass transport. However, the impact of the individual processes on the mass transport needs better understanding. One promising approach that can shed light on these processes is Fluorescence Lifetime Imaging Microscopy (FLIM), as it can capture both spatial and temporal concentration changes near an electrode surface.

In Chapter 3, we introduce 1-methyl-7-amino quinolinium-based fluorescent pH probes as new dyes for FLIM, enabling pH measurements under electrolyzer-relevant conditions (pH 8-13). These probes are highly photostable, water-soluble, and have fluorescence lifetimes of up to 11.5–13 ns, while showing limited sensitivity to temperature

and common ions in aqueous environments. Our experiments demonstrate that these probes can capture chemical and mass transfer processes with a spatial resolution of 4  $\mu$ m and a temporal resolution of 3 frames per second at low probe concentrations (0.1 mM). Additionally, the modular design of these probes allowed us to extend the pH sensitivity from pH 5 to 13.5, and leaves room for development of more dyes.

We apply FLIM and micro-Particle Image Velocimetry ( $\mu$ PIV) to investigate bubbleinduced mass transport at hydrogen evolving electrodes in Chapter 4. Using FLIM, we observe that bubble detachment at a Pt wire electrode significantly reduces the boundary layer thickness. Additionally,  $\mu$ PIV allows us to measure velocity profiles around bubbles at a Ni plate electrode, which we then integrate into a mass transport model. These two experiments both show that bubble detachment and wake flow have substantial effects on mass transport enhancement. Interestingly, we also observed that 'single bubble' events where a bubble grows and detaches without interference from nearby bubbles, are rare at vertical electrodes. Even at low current densities (< 5 mA cm<sup>-2</sup>), wake flows from neighboring bubbles frequently disturb the surrounding electrolyte.

Finally, we combine pressure swings and bubble-induced mass transport in Chapter 5. We use fast pressure swings (50 Hz, 1.2 bar) to enhance mass transport in an aqueous  $CO_2$  electrolyser, generated with a vibratory pump typically found in coffee machines. The pressure pulses result in vibrating bubbles and flow circulations in the electrolyte, which allow us to reach a limiting current density of 87 mA cm<sup>-2</sup> towards  $CO_2$  reduction products. This is an order of magnitude higher compared to H-cell systems and three times higher compared to an electrolyser where the pulses have been damped out. The limiting current density can be increased even further at higher peak-to-peak pressure amplitudes or pump frequencies, which we show through a PIV and an order-of-magnitude scaling analysis. While promising, some challenges still remain if a pressure pulsed  $CO_2$  electrolyser would be upscaled, such as pump energy consumption, contamination and heating, and pressure wave damping.

All things considered, the movement of bubbles is the key factor that distinguishes bubbles from having a positive or a negative impact on electrolysers. We believe that innovative electrode designs and innovative processes could make use of this movement. This could bring electrolysis processes one step closer to being cost-competitive with traditional fossil fuel based processes.

## SAMENVATTING

De opwekking van hernieuwbare energie bereikte in 2023 een recordhoogte: 29% van alle elektriciteit op aarde kwam uit groene bronnen. Elektriciteit zal fossiele brandstoffen echter niet volledig kunnen vervangen. Schommelingen in de opwekking van zonne- en windenergie vereisen extra oplossingen om in alle weersomstandigheden aan de energievraag te voldoen. Daarnaast moet er elektrische energie worden omgezet naar chemische verbindingen om chemicaliën te leveren voor plastics, kunstmest, staal, enz. Elektrolyse – in het bijzonder de elektrolyse van water en  $CO_2$  – biedt hier een veelbelovende oplossing door groene elektriciteit om te zetten in brandstoffen en kleine basismoleculen. Ondanks dat elektrolyseprocessen veelbelovend zijn voor de energietransitie, zijn ze momenteel nog niet economisch rendabel.

Dit proefschrift richt zich op de rol van gasbellen op de *performance* van elektrolyse processen. De vorming van gasbellen is onvermijdelijk in de meeste elektrolysers. Dit is omdat veelvoorkomende elektrolyseproducten (bv.  $H_2$ ,  $O_2$  of CO) slecht oplosbaar zijn in water. Een potentiële manier om de energiekosten van elektrolyse te verlagen, is door het gedrag van gasbellen in het systeem te beïnvloeden. Hierdoor kunnen we de celspanning verlagen en het massatransport verbeteren, waardoor er gewerkt kan worden op hogere stroomdichtheden. Dit kan helpen om de kosten van elektrolyse te verlagen, waardoor het beter kan concurreren met processen op basis van fossiele brandstoffen.

Gasbellen verhogen de celspanning van elektrolysers omdat ze de geleidbaarheid van het elektrolyt verminderen en delen van het elektrodeoppervlak blokkeren. Om de negatieve effecten van gasbellen te verminderen, introduceren we een *zero-gap* alkaline water elektrolyser die werkt met een periodieke *pressure swing* om gasbellen te verwijderen (hoofdstuk 2). Deze drukgolf creëert een toestand van de elektrolyser met en zonder gasbellen, waardoor we de effecten van gasbellen op de celspanning *in situ* kunnen meten. De geometrie van de elektrode en de geleidbaarheid van het elektrolyt bleken de belangrijkste eigenschappen die spanningsverliezen door gasbellen bepalen, terwijl de effecten van de werkdruk tussen 2 en 5 bar beperkt zijn. Daarnaast kunnen pressure swings ook worden gebruikt om de gemiddelde celspanning te verlagen. Het lukt ons om de irreversibele energieverliezen (d.w.z. als gevolg van overpotentialen) met 5% te verminderen bij een elektrolyser met 1 M KOH, 30 °C en nikkel foam elektroden. Tot slot laten we met behulp van een model zien dat perforated plate elektroden bij een elektrolyt met hoge geleidbaarheid (80 °C, 30 massa-% KOH) tot zeer kleine belspanningsverliezen leiden. Dit maakt de pressure swing minder effectief onder deze omstandigheden.

Ondanks de negatieve effecten op de celspanning, kunnen gasbellen elektrolysers ook ten goede komen. De groei, coalescentie en verplaatsing van bellen dragen bij aan het massatransport bij de elektrode. De invloed van deze afzonderlijke processen op het massatransport moet echter beter worden begrepen. Een veelbelovende technologie die licht kan werpen op deze processen is Fluorescence Lifetime Imaging Microscopy (FLIM). Hiermee kunnen concentratieveranderingen zowel in de tijd als in de ruimte bij het oppervlak van een elektrode worden gemeten.

In hoofdstuk 3 introduceren we fluorescerende pH-probes gebaseerd op 1-methyl-7-amino quinolinium. Deze nieuwe FLIM probes maken pH-metingen van pH 8 tot 13 mogelijk, wat relevante omstandigheden voor elektrolysers zijn. Deze probes zijn zeer fotostabiel, oplosbaar in water en hebben een fluorescentielevensduur van 11.5-13 ns. Bovendien worden ze niet sterk beïnvloed door temperatuur en veelvoorkomende ionen. Onze experimenten tonen aan dat deze probes chemische en massatransportprocessen kunnen vastleggen met een ruimtelijke resolutie van 4  $\mu$ m en een tijdsresolutie van 3 frames per seconde bij lage probeconcentraties (0.1 mM). Bovendien konden we door het modulariteit van deze probes de pH-gevoeligheid uitbreiden van pH 5 tot 13.5 en is er nog ruimte voor verdere ontwikkeling.

In hoofdstuk 4 gebruiken we FLIM en micro-Particle Image Velocimetry ( $\mu$ PIV) om massatransport door gasbellen aan waterstof-elektroden te onderzoeken. Met FLIM zien we dat het loslaten van bellen bij een platinadraadelektrode de dikte van de grenslaag aanzienlijk vermindert. Daarnaast kunnen we met  $\mu$ PIV snelheidsprofielen in het elektrolyt rondom gasbellen meten bij een nikkel plaatelektrode. Deze snelheidsprofielen implementeren we vervolgens in een massatransportmodel. Deze twee experimenten tonen aan dat tijdens het loslaten van bellen en de *wake flow* het massatransport het beste is. We hebben ook geobserveerd dat een 'enkele bel', waarbij een bel groeit en loslaat zonder invloed van nabijgelegen bellen, zeldzaam is bij verticale elektroden. Zelfs bij lage stroomdichtheden (< 5 mA cm<sup>-2</sup>) verstoort de wake flow van naburige gasbellen vaak het omringende elektrolyt.

Tot slot combineren we in hoofdstuk 5 pressure swings en door bellen veroorzaakt massatransport. We gebruiken snelle drukpulsen (50 Hz, 1.2 bar) om het massatransport te verbeteren in een CO<sub>2</sub> elektrolyser. Deze pulsen zijn opgewekt met een vibratiepomp die gewoonlijk in koffiezetapparaten te vinden is. De drukpulsen resulteren in trillende bellen en stromingscirculaties in het elektrolyt waardoor we een *limiting* stroomdichtheid van 87 mA cm<sup>-2</sup> naar CO<sub>2</sub>-reductieproducten kunnen bereiken. Dit is een orde van grootte hoger vergeleken met H-cel systemen en drie keer hoger vergeleken met een wanneer de drukpulsen worden gedempt. De *limiting* stroomdichtheid kan nog verder worden verhoogd bij hogere piek-tot-piek drukamplitudes of pompfrequenties. Dit laten we zien aan de hand van een analyse met PIV experimenten en een orde-van-grootte schaling. Hoewel dit systeem veelbelovend is, zijn er nog enkele uitdagingen om een drukgepulseerde CO<sub>2</sub> elektrolyser op te schalen. Bijvoorbeeld het energieverbruik van de pomp, effecten van verontreiniging in het elektrolyt, en demping van de drukgolven.

Al met al is de verplaatsing van bellen de belangrijkste factor die bepaalt of ze een positieve of negatieve invloed hebben op elektrolysers. Nieuwe elektrodeontwerpen en/of -processen die de beweging van gasbellen benutten, zouden elektrolyseprocessen kunnen verbeteren. Wij geloven dat dit elektrolyseprocesses een stap dichter bij de kosten van traditionele fossiele brandstof-gebaseerde processen kan brengen.

# 1

### **INTRODUCTION**

#### 1.1. THE NEED FOR WATER AND CO<sub>2</sub> ELECTROLYSIS

The previous year, 2023, broke many climate records[1]. The global average temperature was the highest since the beginning of temperature data measurements (1850)[2]. This resulted in more extreme weather events[3], such as forest fires[4], floods[5] and record braking heat waves[6]. The global temperature increase is mainly driven by the rapidly increasing concentrations of  $CO_2$  (to 419 ppm) and  $CH_4$  (to 1902 ppb)[2]. The high  $CO_2$  and  $CH_4$  concentrations are a result of the consumption of fossil fuels by humans, which remains large to this day.

Luckily 2023 was not only characterized by lows, we also globally produced the largest amount of renewable electricity ever recorded[7]. Of all generated power, 29% was produced from renewable sources (hydro, wind, solar and bio-energy) to power houses, electronics, transport and the industry. Many regions, like California, Spain, Portugal and Costa Rica, even achieved 100% renewable power on windy and sunny days[8–11]. However, even if we can build a sufficiently large renewable energy capacity, electrical energy cannot fully replace fossil fuels. Three major challenges for switching to renewable energy are discussed below (Figure 1.1):

1. Intermittent energy sources: Renewable energy consists for a large part of wind and solar energy[7], energy sources which are dependent on the time of the day and the local weather conditions. The corresponding mismatch in electricity production rates and consumer demands[12] requires large scale electricity storage to ensure electricity is available on cloudy or windless days[13]. Batteries perform well for short term energy storage, but are not suitable for longer durations (weeks/months)[14]. Hydrogen from water electrolysis is often suggested as a long-term storage alternative[14]. This hydrogen can be stored for long durations, either by compressing, cryogenic liquid hydrogen, metal hydrides or other hydrogen carriers [14], [15]. At moments of insufficient solar or wind power, the stored hydrogen can then be turned back into electricity using fuel cells.



2



Figure 1.1: Renewable energy cannot stop climate change without solving major challenges. Water and  $CO_2$  electrolysis could be the tools to overcome some of those barriers. (Original artwork by Nik Heemskerk)

- 2. Need for carbon based fuels and chemicals: Fossil fuels are used in the production of most consumer products. Plastics[16], small organic chemicals[17–19], solvents[20] and lubricants[21] are just a few of those essential products. Additionally, some forms of transport, such as long distance flights[22] and heavy-duty transport[23], cannot be powered by electricity, as the energy density of batteries is just not high enough. Sustainable alternatives to electric energy are needed to replace fossil-based fuels and chemicals. Electrolysis can be used to make e-chemicals and e-fuels where batteries cannot fulfil the job[15, 24–26]. With techniques such as CO<sub>2</sub> electrolysis, water electrolysis and the Fischer-Tropsch process, one can produce almost all carbon based chemicals from renewable energy[24, 26].
- 3. **Overloaded electricity grids:** Electric cars, heat pumps, and other essential elements of the energy transition result in a rising demand for electricity. Unfortunately, in many countries (including the Netherlands) the progress on grid expansion is slower than the growing demand for electricity[27]. This results in overloaded electricity grids which prevent the efficient distribution of electricity to consumers[28]. The transportation of hydrogen from electrolysis via pipelines and its subsequent utilization (for example using fuel cells at the destination), could alleviate the strain on the grid[29, 30]. On top of that, the transport of H<sub>2</sub> through pipelines has a larger capacity and lower MW km<sup>-1</sup> cost than typical kV electrical transmission lines[31].

To conclude, electrolysis processes can provide a solution by converting renewable electrical energy into molecular bonds. Given their versatility and technical readiness, the main target molecules for electrolyzers are  $H_2$  from water electrolysis and small carbon molecules (like CO,  $C_2H_4$ , HCOOH, etc) from CO<sub>2</sub> electrolysis. These can act as fuels directly, or as building blocks for more complex molecules in the chemical industry.

Although electrolysis processes are very promising for the energy transition, their costs are currently still too high compared to fossil fuel-based processes[26]. The two largest contributors to the high price of electrolysis are: Electricity consumption and Capital expenses (CAPEX)[32]. To minimize the electricity costs, the operating voltage of electrolyzers needs to be as low as possible. The CAPEX can be reduced when operating electrolyzers at higher current densities (i.e., making them more productive) because fewer and/or smaller electrolyzers can be used to produce the same amount of products.

The International Renewable Energy Association (IRENA) concluded that higher current densities are the most important parameter to reduce the price of green hydrogen; even tripling the current density for alkaline electrolyzers is targeted for 2050 without compromising on the energy efficiency[33]. However, at higher current densities more hydrogen and oxygen gas bubbles will form, and their corresponding ohmic losses become a significant issue. This is because the contribution of gas bubbles to the energy consumption scales linear or super-linear with current density, while reaction kinetics scale sub-linear with current density.

In this thesis, I will focus on the role of **gas bubbles** in water and  $CO_2$  electrolyzers, and their impact on both the electricity consumption and achievable current densities. In the rest of this chapter I will discuss the negative effects gas bubbles on the cell voltage and the positive effects of gas bubbles on the mass transport. Finally, the effect of pressure on gas bubbles will be discussed, which can be used to control gas bubble behaviour.

#### **1.2.** How do gas bubbles influence the cell voltage of electrolyzers?

In a cost-effective electrolyzer, the cell voltage ( $E_{Cell}$ ) should be as low as possible, while the electrical current (I) should be as high as possible. Unfortunately gas bubbles inside electrolyzers can significantly increase the cell voltage[34, 35]. To explain the effect of gas bubbles on  $E_{Cell}$ , I will use an alkaline water electrolyzer as example. A typical alkaline water electrolyzer consists of two nickel-based electrodes in concentrated KOH, separated by a porous separator (Figure 1.2A)[36]. When an electrical current is applied to these electrodes, H<sub>2</sub> and O<sub>2</sub> bubbles will form as a result of the following two reactions:

Cathode	$2 H_2 O + 2 e^- \longrightarrow H_2 + 2 O H^-$	$E^0 = 0.00 \mathrm{V} \mathrm{vs} \mathrm{RHE}$	(1.1)
---------	---	--	-------

Anode 
$$4 \text{OH}^- \longrightarrow \text{O}_2 + 2 \text{H}_2 \text{O} + 4 \text{e}^ E^0 = 1.23 \text{ V vs RHE}$$
 (1.2)

The voltage difference between these two reactions,  $E_{Cell}^0$ , is 1.23 V, is the standard potential difference for water splitting. This is the voltage at which the reaction starts to take place. However, in a real alkaline electrolyzer the required  $E_{Cell}$  is higher[34, 35]:

$$E_{\text{Cell}}(j) = E_{\text{Cell}}^0 + j\frac{L}{\kappa} + \eta_{\text{Cat}}(j) + \eta_{\text{An}}(j) + jr_{\text{Sep}} + IR_{\text{Circuit}}$$
(1.3)

Here  $E_{\text{Cell}}$  (in V) is a function of current density j (A cm<sup>-2</sup>), L is the distance between the electrodes in cm,  $\kappa$  is the effective electrolyte conductivity in S cm<sup>-1</sup>,  $\eta_{\text{Cat}}$  and  $\eta_{\text{An}}$ are the activation overpotential of the cathode and anode reactions in V,  $r_{\text{Sep}}$  is the area resistance of the membrane or separator in  $\Omega$  cm<sup>2</sup> and  $R_{\text{Circuit}}$  is the resistance of the electrical wires and connection in  $\Omega$ . Even though gas bubbles are not directly visible in this equation, they do affect four terms in equation 1.3.



Figure 1.2: A. Schematic representation of an alkaline electrolyzer B. Gas bubbles increase the electrolyte resistance C. Gas bubbles on an electrode can cause high local current densities D. Qualitative breakdown of  $E_{Cell}$  inside a zero-gap alkaline water electrolyzer, adapted from Haverkort and Rajaei (2021)[34].

• Figure 1.2B shows the effect of gas bubbles on the electrolyte conductivity. Gas bubbles block the path of least resistance, which increases the distance that  $OH^-$  ions have to travel. This reduces the effective electrolyte conductivity  $\kappa$ . The effect of bubbles on the conductivity is commonly expressed with the Bruggeman equation[37]:

$$\kappa = \kappa_0 \left( 1 - x_g \right)^{1.5} \tag{1.4}$$

Where  $\kappa_0$  is the electrolyte conductivity without gas bubbles and  $x_g$  is the gas fraction in the liquid between anode and cathode. These losses can be minimized

by making the distance between electrodes (*L*) as small as possible. Such a design, also called *zero-gap*, typically has two electrodes pressed against the separator[38].

• When gas bubbles stick to the electrode surface, they can also increase the electrode overpotential,  $\eta_i$ . These bubbles block a part of the active area of an electrode, which result in a small area of the electrode being subject to higher current densities (Figure 1.2C). Assuming that the electrode overpotentials are in the Tafel regime, the overpotential for an electrode that is covered with gas for fraction  $\epsilon_g$  can be calculated with[34, 37, 39]:

$$\eta_{i}(j) = b_{i} \log\left(\frac{j}{j_{i0}(1 - \epsilon_{g})}\right)$$
(1.5)

Here,  $\eta_i$  is the electrode overpotential,  $b_i$  is the Tafel slope ( $b_i = RT/(\alpha_i F)$ ) with *R* as the ideal gas constant, *T* as temperature in K,  $\alpha_i$  the charge transfer coefficient, *F* the Faraday constant and  $j_{i0}$  exchange current density of electrode i.

• Finally, even *r*<sub>Sep</sub> can increase if bubbles stick to the membrane or if gas enters porous separators[40]. The separator resistance is approximately inverse proportional to the available surface area, making the effect:

$$r_{\rm Sep} = \frac{r_{\rm Sep}^0}{1 - \epsilon_g} \tag{1.6}$$

In which  $r_{\text{Sep}}^0$  is the separator resistance without gas bubbles.

To conclude, gas bubbles have a large effect on  $E_{Cell}$  in alkaline water electrolyzers. This can also be seen in the work of Haverkort and Rajaei[34], where bubbles are one of the main contributions to the cell voltage, even in a zero-gap design (Figure 1.2D). A low cell voltage can therefore only be achieved if gas bubbles are handled effectively[41], which is confirmed by the exceptional performance of bubble-free systems. Both capillaryfed electrolyzers[42] and Polymer Electrolyte Membrane (PEM) electrolyzers[43] can reach 2 to 10 times higher current densities at the  $E_{Cell}$ , compared to their two-phase alkaline electrolysis counterpart.

#### **1.3.** BUBBLE-INDUCED MASS TRANSPORT IN ELECTROLYZERS

Up to now, I only discussed the negative influences of gas bubbles on the  $E_{Cell}$ . However, the movement of gas bubbles inside an electrolyzer also create convection. This convection can improve the heat and mass transport from and to the electrode (Figure 1.3A). For gas evolving electrodes, the convection is created close to the electrode surface, where the mass transport is usually needed the most. I will discuss this "bubbleinduced transport" with aqueous electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R) as an example[44]:

Cathode $CO_2(aq) + H_2O + 2e^- \longrightarrow CO + 2OH^ E^0 = -0.106 \text{ V vs RHE}$ (2)	(1.7)
--	-------

Anode 
$$4 \text{OH}^- \longrightarrow \text{O}_2 + 2 \text{H}_2 \text{O} + 4 \text{e}^- \quad E^0 = 1.23 \text{ V vs RHE}$$
 (1.8)

1

The CO<sub>2</sub>R process is mainly limited by low current densities. For example, on a flat silver electrode the current densities are typically limited to only 5-10 mA cm<sup>-2</sup> [45, 46]. Even on electrodes with a very high selectivity towards CO[47–49] the maximum obtainable current density is around 20 mA cm<sup>-2</sup>. This is because CO<sub>2</sub>R is strongly limited by mass transport, as CO<sub>2</sub> has slow diffusion  $(1.91 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1})$  and a low solubility in water (0.032 mol L<sup>-1</sup> at 25 °C, and 1 bar). Increasing the current beyond this limiting current density ( $j_{\text{lim}}$ ) will result in H<sub>2</sub> evolution, which greatly reduces the energy efficiency for carbon-based products[50, 51]. To increase  $j_{\text{lim}}$ , the diffusion boundary layer thickness ( $\delta$ ) needs to be reduced as much as possible (Figure 1.3A). The relationship between  $j_{\text{lim}}$  and  $\delta$  is described by the following equation:

$$\frac{j_{\rm lim}}{nF} = -D\left(\frac{{\rm d}c}{{\rm d}x}\right)_{x=0} \sim -D\frac{c_{\rm Bulk}}{\delta} \tag{1.9}$$

Here n is the amount of electrons in the reaction, F is the Faraday constant and  $-D(dc/dx)_{x=0}$  the diffusive flux towards the electrode surface. This term can be linearly approximated to obtain  $\delta$ , where  $c_{\text{Bulk}}$  is the concentration of CO<sub>2</sub> in the bulk electrolyte.



Figure 1.3: **A.** Effect of gas bubbles on the diffusion boundary layer thickness in  $CO_2R$  **B.** Example of good gas bubble control in  $CO_2R$  (Figure inspired by Burdyny et al.[52]) **C.** Order of magnitude comparison of limiting current density ( $j_{lim}$ ) on different electrodes. References: Flat silver electrodes[45, 46], Catalysts with high CO selectivity (Ag on Zn dendrites[47], Au<sub>25</sub> clusters[48] and Ag nanoparticles[49]), Nano-structured electrodes[52].

Gas bubbles, as shown by Burdyny et al.[52], are an effective tool to reduce the diffusion boundary layer thickness. In Burdyny's work, gas bubble sizes were reduced by employing a nanostructured catalyst. The large amount of small bubbles caused more mixing events, which improved the mass transport significantly (Figure 1.3B)[52]. The  $j_{lim}$  obtained with this bubble-induced mass transport surpassed a flat Ag electrode by an order of magnitude, and even exceeded the  $j_{lim}$  of highly selective catalysts[47–49] by more than twice (Figure 1.3C).

To wrap up, gas bubbles are an essential part in the optimization of electrochemical processes and can help to achieve larger current densities. Although the focus of this thesis is mainly on the reduction of water and CO<sub>2</sub>, the findings will apply to any gas-evolving electrochemical device, since all gases will behave similarly.

#### **1.4.** CONTROLLING GAS BUBBLES WITH PRESSURE

Having established that gas bubbles can have either a negative impact on  $E_{\text{Cell}}$  or can increase the productivity of electrolyzers through bubble-induced mass transport, it is essential to actively control gas bubbles to our advantage. Figure 1.4A shows forces acting on a gas bubble that can be tuned by operational modes or electrode modifications. By adjusting one of these parameters, e.g. with an external centrifugal force[53, 54], by applying a strong shear flow [55] or by making the electrode more hydrophobic[56–58], we can gain control over how the gas bubbles inside the electrolyzer behave.

The pressure is a noteworthy case, as doubling the pressure will result in half the volume of produced gas ( $P \propto V_{gas}^{-1}$ ). This has already been widely used in industrial alkaline electrolyzer stacks (operating under 10-50 bar pressure) to reduce  $E_{Cell}$  and downstream compression costs[40, 59]. However, while a static high pressure will reduce the rate of gas bubbles that are formed, there can still be a considerable amount of gas bubbles inside the system, as the forces acting on the gas bubbles remain unchanged.



Figure 1.4: **A.** Examples of properties that dictate how a gas bubble behaves, and methods that were used to influence these properties. ( $F_{\text{Surf}}$  = Surface force,  $F_{\text{B}}$  = Buoyancy force, P = pressure) **B.** Changes in the pressure will cause gas bubbles to grow and shrink. **C.** Typical pressure wave frequencies for methods that are used to control gas bubbles inside electrolyzers. The region between  $10^{-2}$  Hz to 1 kHz remains relatively unexplored. References: Supergravity[60, 61], Centrifugal forces[53, 54, 62], Ultrasound[63–65], Pressure swings[66], Surfactants[67–69], Hydrophobic electrodes[56–58].

On the other hand, a dynamic pressure can impact the forces acting on a bubble (Figure 1.4B). By adjusting the pressure in the system, the size of gas bubbles can be changed. This phenomenon has primarily been studied at high frequencies (kHz-MHz) with ultrasound[63–65]. However, work from our group has shown that slower pressure changes can also be used to remove gas bubbles from the electrode[66]. By periodically reducing the pressure for a short time (5 s) at intervals of 50-3000 s, gas bubbles will grow and are pulled off the electrode by the generated convection and additional buoyancy force.

Even though the initial pressure swing research showed promise, the best results were found with the fastest cycles. Unfortunately, the frequency was limited to 0.02 Hz by the setup. electrolyzers operating under ultrasound have also shown improved mixing and bubble detachment. However, ultrasonic waves dampen quickly, making them difficult to apply to scaled-up electrolyzers. In this thesis, I will apply pressure waves in the intermediate range  $(10^{-2} \text{ Hz to 50 Hz})$ . This range has the promise to enhance the effects of previous pressure swing work while maintaining the possibility for scale-up (Figure 1.4C).

#### **1.5.** Thesis outline and research questions

Good gas bubble management is essential for electrolysis processes, as gas bubbles have both negative effects on  $E_{Cell}$  and positive effects on the mass transport. However, due to the stochastic nature of gas bubbles it can be difficult to make general statements on bubble effects. The wide variety of electrolyzer configurations and electrode geometries studied across the scientific community adds to this complexity. Hence, there is a need for new methods to quantify bubble effects in electrolyzers and at electrodes, which can allow us to study bubble effects on a case by case basis.

In this thesis I will provide new methods to determine the effects of gas bubbles on the cell voltage, show how large the effects of gas bubbles are on alkaline water electrolyzers and aqueous-based  $CO_2$  electrolysis, and finally try to control gas bubbles inside electrolyzers with  $10^{-2}$  to 100 Hz pressure variations. The following research questions (RQ) will be answered in this thesis:

- **RQ1:** How large is the effect of gas bubbles on the cell voltage in a zero-gap alkaline water electrolyzer? (**Chapter 2**)
- **RQ2:** How much can the cell voltage be reduced when gas-bubbles are removed from a zero-gap alkaline water electrolyzer with a pressure swing (5-180 s, 1-2 bar)? (**Chapter 2**)
- **RQ3:** What fluorescent pH probe is suitable to study mass transport at a gas-evolving electrode with Fluorescent Lifetime Imaging Microscopy (FLIM)? (**Chapter 3**)
- **RQ4:** What microprocesses during gas bubble evolution are the biggest contribution to bubble-induced mass transport at electrodes? (**Chapter 4**)
- **RQ5:** How much can the limiting current density of aqueous CO<sub>2</sub> reduction be improved with fast pressure pulses (50 Hz, 1-2.5 bar)? (**Chapter 5**)

These questions are answered throughout the thesis in the following chapters. Chapter 2 reports a pressure swing-assisted zero-gap alkaline water electrolysis setup, which will be used both for understanding the effects of gas bubbles on  $E_{Cell}$  and to mitigate those effects by bubble removal. In Chapter 3, I report a series of new quinolinium pH probes for Fluorescence Lifetime Imaging Microscopy (FLIM) that will allow us to study the mass transport at gas-evolving electrodes. In Chapter 4, I will investigate the mass transport during gas evolution at an electrode with micro Particle Imaging Velocimetry (µPIV) and FLIM. In Chapter 5, I will apply a fast pressure pulsed flow (50 Hz, 1-2.5 bar) to boost the limiting current density in an aqueous electrolyzer. Chapter 6 will show overarching conclusions and opportunities for future research.

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## 2

## GAS BUBBLE REMOVAL FROM ELECTROLYZERS WITH A PRESSURE SWING



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To make green hydrogen more economically attractive, the energy losses in alkaline electrolysis need to be minimized while operating at high current densities  $(1 \, A \, cm^{-2})$ . At these current densities the ohmic resistance and gas bubbles effects contribute largely to the energy losses. To mitigate the gas bubbles losses, we demonstrate, for the first time, a pressure swing to remove gas bubbles in a zero-gap alkaline water electrolyzer. The pressure swing leverages the ideal gas law to increase the volume of gas in the system periodically, for a short duration (<2 s). This temporal volume increase effectively removes bubbles from the electrolyzer. We show that pressure swing can be used to measure the effect of bubbles on the ohmic resistance (R<sub>Bubbles</sub>). Our results reveal that foam electrodes have a significantly larger  $R_{\text{Bubbles}}$  than perforated plate electrodes (1.8  $\Omega$  cm<sup>2</sup> vs 0.3  $\Omega$  cm<sup>2</sup>). The time-averaged cell voltage reduces by 170 mV when applying pressure swings to an electrolyzer operating at 200 mA cm<sup>-2</sup> in 1 M KOH with foam electrodes. The bubble resistance further depends on the electrolyte conductivity (inversely proportional) and is only moderately affected by operating pressure (25% lower when increasing pressure amplitude from 1-2 to 1-5 bar). By implementing these findings in a model, we estimate that the pressure swing could reduce the cell voltage by  $\sim 0.1$  V for an electrolyzer operating at industrial conditions (6 M KOH, 80 °C, 1 A cm<sup>-2</sup>) for foam electrodes. However, for perforated plate electrodes, the compression energy is often larger than the gain in energy efficiency.

#### **2.1.** INTRODUCTION

To limit global warming, fossil fuels need to be phased out as our main source of energy and chemicals[1, 2]. Green hydrogen is indispensable for the fossil-free production of fertilizers, steel and chemicals.[3] IEA estimates that we will need 80 Mton  $yr^{-1}$  of green hydrogen production by 2030 to be on track to net zero CO<sub>2</sub> emissions by 2050[4], which is enormous compared to the predicted installed 0.45 Mton  $yr^{-1}$  capacity by the end of 2023[5].

To produce such large amounts of green hydrogen, we can use alkaline electrolysis[6]. Alkaline electrolysis benefits from its scalability as it uses abundant metal catalysts like iron and nickel, which is mandatory if we consider the required scale of hydrogen production[6, 7]. Unfortunately, alkaline electrolysis is not economically attractive yet. The US department of energy calculated that the costs need to be reduced by 80% to reach their target of 1 dollar per 1 kg H<sub>2</sub>[8]. These large cost reductions can only be achieved when the energy efficiency of alkaline electrolysis improves significantly at high current densities (>1 A cm<sup>-2</sup>)[9].

At high current densities the contribution of energy losses shifts towards ohmic losses (which scale linearly with current) and losses due to gas bubbles (which scale linearly or even more than linearly)[10–12]. The latter originates from hydrogen and oxygen bubbles that block the active sites on the electrodes and reduce the conductivity of the electrolyte solution[13–15]. This causes large energy losses, as the bubbles can take up more than 50% of the volume of the electrolyzer[16].

Ohmic losses can be mitigated to some extent by reducing the inter-electrode distance. This is why nowadays a large fraction of alkaline electrolyzers are designed with an (almost) zero-gap design[9, 17]. This design requires porous electrodes to ensure water and gas transport remains possible. Electrode geometries are that are typically used are metal foams[18, 19], expanded meshes[20] and perforated plates[16, 21]. However, a zero-gap configuration still suffers from bubbles, since gas gets stuck in the electrode pores and reduces the electrochemically active surface area[16, 22]. Not only do gas bubbles increase the ohmic resistance, they can also mechanically damage catalyst surfaces[23] and fluctuations in the electrical potential due to bubbles can lead to gradual degradation of the catalyst layer[24, 25]. Creative methods to avoid and remove gas bubble are therefore crucial to fully optimize alkaline electrolyzers. Gas bubble-mitigation strategies can be divided into three main approaches: Reducing gas bubble effects at the electrode microstructure level, electrode geometry level and at the process level.

Electrodes can be optimized at the microscale by creating nano- and micro-structured electrodes [26] (such as nanoneedles [27] and striped-pattern superlattices [25]). The sharp interfaces reduce the adhesion forces of gas bubbles, which results in a much faster release and thus 2-100x reduction in gas bubble sizes [25, 27]. Additionally, electrodes with small hydrophobic have been synthesized to locally induce nucleation and collect gas, to keep the remaining electrode area gas-free [28–30]. However, it is highly challenging to make such electrodes stable under high current densities at the hostile conditions of 30wt% KOH and 80 °C for hundreds or even thousands of hours [31].

The macroscale electrode geometry can also mitigate the adverse effects of gas bubbles. The optimal geometry is a trade-off between a high electrochemically active surface area (ECSA) while keeping large enough pores to prevent bubble trapping in the pores. Previous work showed that mesh and foam electrodes with the highest ESCA can be outperformed by electrodes with a lower ECSA but large enough pores for bubble release[18, 32, 33]. Although, shape optimization and the use of non-standard electrode geometries[19, 34, 35] could result in even better gas-bubble mitigation, the complexity and trade-off with active surface area still limits the effectivity of this route for gas bubble mitigation.

On the process level, the electrolyte, operating conditions and cell geometry can be optimized or one can apply external forces to reduce bubble effects. For example, Zhao et al. and others have shown that adding a surfactant to the electrolyte reduces the bubble nucleation energy and enhances bubble removal[23, 36–38]. However, surfactants also cause foaming[27], which will make downstream gas-liquid separation more difficult. Operating the electrolyzer at a higher pressure has minimal impact in zero-gap electrolyzers; the stagnant bubbles ultimately release after reaching sufficient buoyancy, which means the bubble coverage is similar at low or high pressure in steady state[21, 39]. Gas bubble removal can be enhanced to some extent with turbulence promoters[40] or by having a "small-gap" instead of zero-gap[20]. Finally, gas bubbles can also actively be removed by process intensification, such as having an external force field[41–43], centrifugal flow[44], with ultrasound[45–47] or pressure waves[48]. Nevertheless, even with these strategies, gas bubble resistance remains a substantial part of the irreversible energy losses in electrolysis.

We introduce, for the first time, a pressure swing to remove gas bubbles in a zerogap water electrolyzer. A pressure swing leverages the ideal gas law, by temporarily increasing the buoyancy and volume of gas bubbles at lower pressures. In our previous work[48], we showed that the average cell voltage can be reduced by 0.1-0.2 V applying a pressure swing (1-4 bar) periodically to an electrolyzer with a large gap. We have improved the response time of the pressure swing to be able to apply it to a zero-gap electrolyzer. Here, we use the pressure swing to analyse and quantify the effect of gas bubbles on the cell voltage. We demonstrate that the cell voltage is reduced when applying a pressure swing to a zero-gap electrolyzer, and that pressure swings can be leveraged to obtain in-operando information about the gas bubble coverage.

#### **2.2.** METHODS

#### **2.2.1.** Electrochemical cell and materials

Pressure swing assisted electrolysis was performed in a custom-made rectangular Poly(methyl methacrylate) (PMMA) flow cell, see figure 2.1. To achieve high transparency the PMMA was milled with a special diamond mill. The flow channels are 5 mm deep and 25 mm wide, and three polypropylene pillars (6 mm diameter) were added to keep the electrodes in place. The electrodes were either Ni foam (Recemat BV, RCM-Ni4753.005, 0.5 mm thickness, 0.4 mm average pore diameter, 0.952 porosity) or Ni perforated plate (Veco B.V., 0.3 mm thickness, 1.0 mm average pore size, 0.312 porosity). During experiments, the cathode and anode always had the same geometry (e.g. foam/foam). The electrodes have a geometric surface of 40 cm<sup>2</sup> and were pre-treated in situ. We welded two nickel wires to each electrode for electrical contact. The electrodes were separated by a Selemion AHO anion exchange membrane, which was used because of

its good pressure-, gas-crossover- and alkalinity-resistance. EPDM O-rings (3 mm diameter, ERIKS) were used for sealing. The cell was pressure tested for 7 bar.



Figure 2.1: Exploded diagram of the electrolyzer used in the pressure swing assisted electrolysis experiments

#### **2.2.2. PRESSURE SWING EQUIPMENT**

The KOH catholyte and anolyte (45wt% Thermo Scientific, diluted with demineralized water to 0.3, 1, 2, 3 or 6 M) are pumped through the system with peristaltic pumps at 72 mL min<sup>-2</sup> (MasterFlex L/S with 16HP tubing, max pressure 8.5 bar). The maximum pressure in the electrolyzer was controlled at the outlet with two back-pressure regulators (Swagelok, Stainless steel, Kalrez seals) to 2-5 bar. The pressure swing was regulated with solenoid valves (Buschjost 82560 series, Stainless steel) at the inlet (1/4") and outlet (1/2") of the electrolyzer. To achieve a quick pressure response, membrane expansion vessels (Reflex Winkelmann GmbH, Reflex S2) were installed before the inlet solenoid valves. The gas cushion in the expansion vessels was pressurized with nitrogen to the desired operating pressure of the electrolyzer. See figure 2.2 for the process diagram of the system. During high pressure operation, the inlet valve was open and the outlet solenoid was closed, and the liquid is exits the system through the back pressure regulator. The pressure swings were performed in four steps:

- 1. For 0.5 s, all valves are closed.
- 2. For 1 s, the outlet valve is opened. The system is now open to atmosphere and depressurizes. The pump continues pumping, but into the expansion vessel.
- 3. For 0.5 s, all valves are closed.



Figure 2.2: Process diagram of the pressure swing setup, see SI 2.5.1 for the operation scheme of the pressure swing

4. The inlet valve is opened again. High pressure liquid enters the system from the pump and expansion vessel.

This setup results in a pressure response of <1 s to achieve low pressure (step 2) and high pressure (step 4), which is much faster compared to previous work (5 s to low pressure, ~20 s to high pressure)[48]. The pressure was recorded with pressure transmitters (TC-Direct, 716-908) at the in- and outlet of the electrolyzer. The temperature was recorded by a thermocouples in the catholyte bottle and the cathode and anode compartments inside the electrolyzer (TC-Direct), during all measurements the temperature was 23-30 °C.

#### **2.2.3.** Electrochemical measurements

All electrolysis experiments were performed at constant current to ensure a constant gas production rate. The current was controlled with an Ivium XP20 Potentiostat. This was connected to the anode and cathode in a 4-electrode configuration to minimize ohmic losses in the voltage signal. Before every measurement series, the cell was operated at 200 mA cm<sup>-2</sup> for 30 min at atmospheric pressure without a pressure swing. This was both to pretreat the electrodes and saturate the electrolytes with oxygen and hydrogen, to minimize Nernstian effects on the voltage. In all  $\Delta E_{\text{Bubbles}}$  measurements, the experiments were performed from high to low current densities, to minimize the effects of Ni redox reactions and effects from changes in dissolved gas concentration at lower currents.

#### **2.2.4.** CONTROL AND DATA ACQUISITION

The pressure transmitters and thermocouples were read out with a NI-9207 and NI-9213 modules respectively and the solenoid valves were controlled with a NI-9482 relay module. The setup was controlled with a custom Labview script and the data was processed with in Python. All scripts are available on the Zenodo repository.

#### **2.3. RESULTS AND DISCUSSION**

We developed a pressure swing to remove hydrogen and oxygen gas bubbles from a zero-gap alkaline water electrolyzer. First, the concept of the pressure swing will be demonstrated and used to quantify the effects of gas bubbles on our zero-gap electrolyzer setup. Then pressure swing assisted electrolysis will be evaluated experimentally and with a simple analytical model.

#### **2.3.1.** PRESSURE SWING CONCEPT IN A ZERO-GAP ELECTROLYZER

The gas production in a zero-gap alkaline electrolyzer is largest near the electrode separator interface[16], as the ionic travel distance between cathode and anode is the shortest here. A zero-gap configuration always has some small gap between the electrode and the separator. This is because the electrodes are not perfectly flat or the cell is compressed in-homogeneously[16, 20] (see figure 2.3Left). As there is no easy path to release into the bulk electrolyte, gas bubbles tend to accumulate in this gap and in the pores of the electrode. The pressure swing is a method to remove these gas bubbles in three stages (figure 2.3):



Figure 2.3: Left/Middle top. Graphical representation bubble removal of a pressure swing in a zero gap alkaline water electrolyzer. Step 1. High pressure operation, Step 2. Low pressure step of the pressure swing, Step 3. Compression back to high pressure. Middle bottom. Images of oxygen bubbles on a Ni perforated plate anode during the pressure swing, 80 mA cm<sup>-2</sup> Right. Voltage response to the pressure swing between 1 – 4 bar, at 200 mA cm<sup>-2</sup>, 1 M KOH, Ni foam electrodes. Section 2.6 contains videos of the electrodes during a pressure swing

- 1. Default operation at constant current and high pressure. The electrode and cell are saturated with gas bubbles. The cell voltage is high and fluctuating from constant detachment and coalescence of hydrogen and oxygen bubbles.[49]
- 2. The pressure is reduced to atmospheric pressure for 1 s. This causes gas bubbles to expand. Bubbles inside the pores of the electrode are expanded and pushed out into the bulk electrolyte. During the low pressure stage the cell voltage increases, as all gas bubbles expand and further reduce the active electrode area and electrolyte conductivity. During stage 2 the pump is not connected to the electrolyzer and the flow is driven by expanding gas bubbles.
- 3. The electrolyzer reconnected to the pump and pressurized by an inflow of high pressure electrolyte, which recompresses the remaining gas in the system. This flush of electrolyte removes the remaining gas bubbles from the bulk electrolyte. As the electrolyzer continuously produces new hydrogen and oxygen, the system will eventually transition back to stage 1.

To conclude, the pressure swing is an effective method for removing gas bubbles from the electrode surface of a zero-gap alkaline electrolyzer The effectiveness of the bubble removal can be seen in the images in figure 2.3, the videos in section 2.6 and in the voltage response, where most of the fluctuations have disappeared during stage 3. The combination of the pressure pulse and the large flowrate in step 3 is key for good gas bubble removal. Our preliminary experiments have shown that a large flowrate pulse alone is not able to remove all gas, see SI 2.5.2.

**DETERMINING THE OHMIC CONTRIBUTIONS OF GAS BUBBLES (***R*<sub>Bubbles</sub>**)** 

The pressure swing allows us to measure the cell voltage of a electrolyzer in-situ with and without gas bubbles. When comparing the voltage directly after the pressure swing to the steady state voltage, the effects of gas bubbles ( $\Delta E_{\text{Bubbles}}$ ) can be quantified (Figure 2.4A) at the operating pressure, i.e. 4 bar in Figure 2.4A. We acknowledge that  $\Delta E_{\text{Bubbles}}$ could be underestimated because most, but not all, gas bubbles are removed, especially at higher current densities.  $\Delta E_{\text{Bubbles}}$  could also be overestimated as the large inflow of fresh electrolyte could affect the concentration overpotential or induce slight changes in temperature. Swiegers et al. stated in their review article that estimates of bubble overpotentials are rare[12]. Because gas bubbles influence both the local current density and ohmic resistance, it is hard to isolate their contribution from other unrelated contributions to the overpotential. We believe that fast pressure swings, applied to electrolyzers in operando, could be a reliable approach to investigate and isolate bubble overpotentials ( $\Delta E_{\text{Bubbles}}$ ). By installing (micro-)reference electrodes one could even measure  $\Delta E_{\text{Bubbles}}$  on cathode and anode individually.

Figure 2.4B shows the relation between  $\Delta E_{\text{Bubbles}}$  and the current density for a Ni foam electrode, 1 M KOH and a 1-2 bar pressure swing.  $\Delta E_{\text{Bubbles}}$  is almost linear with current density until 150 mA cm<sup>-2</sup>, with an  $R_{\text{Bubbles}}$  slope of 1.8  $\Omega$  cm<sup>2</sup>. The linearity indicates that gas bubbles in a zero-gap Ni foam electrode cause an ohmic resistance, that is independent of the current up to 150 mA cm<sup>-2</sup>. In other words, the rate of gas bubble production in the system does not seem to have a large effect on the bubble



Figure 2.4: A. Cell voltage drop after bubble removal with a pressure swing ( $\Delta E_{\text{Bubbles}}$ ) B.  $\Delta E_{\text{Bubbles}}$  for various current densities (*j*), 1M KOH, 1-2 bar pressure swing, Ni foam. Linear fit until 150 mA cm<sup>-2</sup> of  $\Delta E_{\text{Bubbles}}$  results in a  $R_{\text{Bubbles}}$  (= $\Delta E_{\text{Bubbles}}/j$ ) of 1.8  $\Omega$  cm<sup>2</sup> C. Cell voltage vs time for a 1-2 bar pressure swing, 150 mA cm<sup>-2</sup>, 1M KOH, Ni foam. Linear fits were performed after pressure swing to find the  $dE_{\text{cell}}/dt$ . D. Saturation time after a 1-2 bar pressure swing, 1M KOH, Ni foam electrodes. Averaged over at least 10 pressure swings. Fitted with Eq 2.1 with a  $V_0$  of 0.045 mL cm<sup>-2</sup>.

resistance. We believe this is caused by a saturation of the electrode pores and electrodeseparator gap with gas bubbles, as was also suggested by others[16, 22]. In Figure 2.4B a lower  $\Delta E_{\text{Bubbles}}$  slope is observed at >150 mA cm<sup>-2</sup>. We believe this slope change is a results from the large gas production during the low pressure of the pressure swing. During the low pressure time at 150 mA cm<sup>-2</sup>, 0.029 mL cm<sup>-2</sup> of H<sub>2</sub> gas is formed, which is 60% of the pore volume of the foam. These remaining gas bubbles increase the voltage after a pressure swing, hence  $\Delta E_{\text{Bubbles}}$  is no longer a true representation of the voltage change due to gas bubbles. These points were therefore not included in the  $R_{\text{Bubbles}}$ slope fit.

After the pressure swing, the system will return to a steady state where the electrode pores are saturated with gas bubbles. We calculated this saturation timescale,  $t_{sat}$ , with a linear fit of the cell voltage (Figure 2.4C). Here  $t_{sat} = \Delta E_{Bubbles} / (dE/dt)_{fit}$ .  $t_{sat}$  is inversely proportional to the current density (*j*) (Figure 2.4D). We can further hypothesize that  $t_{sat}$  equals the bubble volume in the porous electrode at saturated conditions ( $V_0$ , in mL cm<sup>-2</sup>) divided by the volumetric gas production rate:
$$t_{\text{sat}} = \frac{V_0}{j \frac{RT}{p n_{02} F}} \tag{2.1}$$

In which *j* is the current density (mA cm<sup>-2</sup>), *R* the ideal gas constant (83.14 mL bar K<sup>-1</sup> mol<sup>-1</sup>), *T* temperature (K), *p* the pressure (bar),  $n_{O2}$  is 4 (the ratio of electrons to oxygen) and *F* the Faraday constant (9.6485 10<sup>7</sup> mC mol<sup>-1</sup>). A least squares fit of the experimental data with Eq 2.1 resulted in a saturated gas volume  $V_0$  of 0.045 mL cm<sup>-2</sup>, which is similar to the specified pore volume of our Ni foam (0.048 mL cm<sup>-2</sup>, SI 2.5.3). In steady operation, we therefore believe that most of the pores in the foam are filled with gas, independent of the current density.

### **EFFECT OF CONDUCTIVITY AND PRESSURE**

To further investigate  $R_{\text{Bubbles}}$  we operated the pressure swing at different electrolyte concentrations and operating pressures. We expect  $\Delta E_{\text{Bubbles}}$  to scale linearly with conductivity, if  $R_{\text{Bubbles}}$  is ohmic in nature.

Figure 2.5A shows  $\Delta E_{\text{Bubbles}}$  for a 1-2 bar pressure swing at different concentrations of KOH. All concentrations show a linear relationship with current density.  $R_{\text{Bubbles}}$  was calculated with a linear fit and scales inversely with electrolyte conductivity (Figure 2.5B and SI 2.5.4), which further suggests that the effect of gas bubbles is mainly ohmic. Only at 0.3 M KOH other phenomena start to affect the  $\Delta E$  after a pressure swing, such as temperature difference from ohmic heating and the concentration overpotential[20]. At 6 M KOH,  $R_{\text{Bubbles}}$  is significantly lower than in an electrolyzer with a 10 mm gap[48] but still substantial: 0.63  $\Omega$  cm<sup>2</sup> for a zero-gap system (this work) vs 0.91  $\Omega$  cm<sup>2</sup> for a gap system (Bakker et al. 2019, SI 2.5.5)[48]. This shows that a zero-gap with foam electrodes only reduces a fraction of the ohmic effects of gas bubbles.

The effect of operating pressure on  $\Delta E_{\text{Bubbles}}$  was determined by changing the high pressure of the pressure swing (2, 3, 4 or 5 bar), while the low pressure was kept at atmospheric (Figure 2.5C). We expect the operating pressure having only a small effect on  $R_{\text{Bubbles}}$  at pressure swing timescales above  $t_{\text{sat}}$ . However, the effectivity of gas bubble removal is improved by the larger pressure difference. We observe that  $\Delta E_{\text{Bubbles}}$  and  $R_{\text{Bubbles}}$  only change by ~25% at a 1-5 bar pressure swing compared to an electrolyzer operating at 1-2 bar (see SI 2.5.4 for  $R_{\text{Bubbles}}$  values), while the pressure and gas bubble formation are 2.5x higher. This is in agreement with the small effect of current density on  $R_{\text{Bubbles}}$ , which shows that the bubble resistance of a flow-by zero-gap electrolyzer is almost independent of the gas production rate. This was also observed in figure 2.4B and in literature[21, 39, 50].

The saturation time,  $t_{sat}$ , also follows Eq 2.1 at higher pressures (Figure 2.5D). Also at higher pressures, the fitted volume  $V_0$  is the same order of magnitude as the pore volume of the electrode. This indicates that the trapped gas volume inside the pores of the foam is independent of pressure. Bubble release at the electrode is therefore key, even for zero-gap configurations. To that end, other electrode geometries than foams, such as electrodes with a larger pore size, could result in a smaller  $R_{\text{Bubbles}}$ .

### **EFFECT OF ELECTRODE GEOMETRY**

Figure 2.6A compares  $\Delta E_{\text{Bubbles}}$  for a 1-2 bar pressure swing in 1 M KOH between foam and perforated plate electrodes.  $R_{\text{Bubbles}}$  is calculated to be 1.8  $\Omega$  cm<sup>2</sup> and 0.3



Figure 2.5: Bubble effects on Ni foam electrodes at different concentrations and pressures **A**.  $\Delta E_{\text{Bubbles}}$  for a 1-2 bar pressure swing at different current densities and KOH concentrations, a linear fit was made to calculate the bubble resistance ( $R_{\text{Bubbles}}$ ) **B**. Effect of KOH concentration on  $R_{\text{Bubbles}}$ . The 6 M KOH case is compared with a 10 mm gap electrolyzer reported by Bakker and Vermaas[48] **C**.  $\Delta E_{\text{Bubbles}}$  for 1-2, 1-3, 1-4 and 1-5 bar pressure swings in 1 M KOH **D**. Saturation time ( $t_{\text{sat}}$ ) for the datapoints in **C**, fitted with Eq 2.1. See SI (2.5.4 for all fitted  $V_0$  and  $R_{\text{Bubbles}}$ 

 $\Omega$  cm<sup>2</sup>, for foam and perforated plate electrodes respectively. By just changing the electrodes, a 6 times reduction in  $R_{\text{Bubbles}}$  can be achieved. This highlights the importance of selecting a suitable electrode geometry for mitigating gas bubble effects. Figure 2.6B and C show the voltage response over time to a pressure wing at 150 mA cm<sup>-2</sup> for the foam and perforated plate electrodes, respectively. After gas bubble removal, the voltage cell voltage for both electrodes is very similar (2.55 - 2.6 V). While the foam electrode has a linear increase in the voltage, the perforated plate seems to have a bi-modal pattern. First a quick increase in the voltage, followed by a slower buildup of voltage. Based on the timescales and the high speed videos (Video S2.12 and S2.13), we believe this is because the electrode membrane gap is quickly filled with gas, after which the 1 mm pores of the perforated plate are filled more slowly. The larger timescale is because H<sub>2</sub> and O<sub>2</sub> bubbles, which have a typical diameter of 50-200 µm[51], can easily escape from the 1 mm pores. This confirms that high surface area electrodes do not always perform best and gas bubble management is equally important.



Figure 2.6: **A.** Comparision of  $\Delta E_{\text{Bubbles}}$  at different current densities (*j*) in Ni foam or perforated plate electrodes, 1-2bar pressure swing and 1 M KOH **B.** Voltage/time response for an electrolyzer with two Ni foam electrodes. Inset is a photo of the electrode. **C.** Voltage/time response for an electrolyzer with two Ni perforated plate electrodes. See SI 2.5.6 for larger photos of the electrode material

The  $R_{\text{Bubbles}}$  of 0.3  $\Omega$  cm<sup>2</sup> measured for a 1 mm Ni perforated plate electrode with the pressure swing, is of the same order of magnitude as simulations by de Groot and Vreman[16]. In addition to this, data from Kraglund shows that foam electrodes can have 4.7x higher  $R_{\text{Bubbles}}$  than perforated plate electrodes[50] (for the comparison with literature, see SI 2.5.5). Although the geometries of his electrodes are different, the order of magnitude increase of  $R_{\text{Bubbles}}$  is similar in our work. This demonstrates that the pressure swing is a suitable method to estimate bubble effects.

# **2.3.2. REDUCING THE CELL VOLTAGE BY APPLYING PRESSURE SWINGS**

We can leverage the pressure swing to reduce the average cell voltage of a zero-gap electrolyzer by removing gas bubbles periodically. Two parameters are varied to optimize the effects of a pressure swing: the high pressure time ( $t_{\text{HP}}$ ) and the operating pressure.  $t_{\text{HP}}$  is the time the electrolyzer operates at a high pressure between two pressure swings (Figure 2.7A and B). Each pressure swing is most effective when the electrodes are saturated with gas bubbles, when  $t_{\text{HP}} \ge t_{\text{sat}}$ . An electrolyzer operating under smaller  $t_{\text{HP}}$  removes gas bubbles more often. Although such a frequent pressure swing can keep the total amount of gas to a minimum, a too high pressure swing frequency compromises



Figure 2.7: 1 M KOH, Ni foam electrodes, 200 mA cm<sup>-2</sup> A. Voltage response to a 1-2 bar pressure swing for two different high pressure times ( $t_{HP}$ ). B. Pressure/time response of A. C. Average cell voltage ( $E_{Cell-avg}$ ) for 1-2 bar pressure swings for different  $t_{HP}$ , compared to if no pressure swing was applied D. Average cell voltage for 1-4 bar pressure swings. Note: The cell voltage of 3.0 - 3.2 V is relatively high compared to similar systems in the literature[16, 20, 52]. We attribute this is to the high ohmic resistance of the Selemion AHO anion exchange membrane, which was used because of its high pressure resistance (12 bar), and the low electrolyte conductivity (1 M KOH at 25-30 °C).

the cell voltage. At low  $t_{\rm HP}$  the electrolyzer will also be more often in the low pressure stage (stage 2 in Figure 2.4A), where gas bubbles are expanded and the ohmic resistance is higher. Moreover, a small  $t_{\rm HP}$  also requires more energy for the more frequent compressions. Similarly, at a high operating pressure, less pressure swings are required (as  $t_{\rm sat}$  increases), but the compression costs of a single swing will be higher (see SI 2.5.7 for an estimation of the compression costs).

In a zero-gap electrolyzer with Ni foam electrodes operating at 1 M KOH, 1-2 bar pressure swings and 200 mA cm<sup>-2</sup>, the average cell voltage can be reduced by 170 mV when applying pressure swings with a  $t_{\rm HP}$  of 5 s (Figure 2.7C). This is a 10% reduction of the energy losses. When the additional compression energy consumption of the pressure swing are included into the cell voltage, the average cell voltage is reduced by 120 mV.

 $t_{\text{sat}}$  is around 7 s at 200 mA cm<sup>-2</sup> and 2 bar (see Figure 2.5D), the optimal pressure swing frequency (5 s in Figure 2.7C) is faster than the saturation time. This is, however,

a trade-off between compression costs and voltage gain. We could not investigate at  $t_{\rm HP}$  lower than 5 s, because our system did not pressurize in quick enough for the next pressure swing. In addition to this, at  $t_{\rm HP}$  < 5 s the required pump energy starts to become excessive and outweighs the gains in efficiency by the pressure swing.

### **EFFECT OF OPERATING PRESSURE**

Figure 2.7C and D show the average cell voltage vs  $t_{\rm HP}$  when operating under a 1-2 or 1-4 bar pressure swing (see SI 2.5.8 for 1-3 and 1-5 bar pressure swings). At all pressures, the improvement of the average cell voltage was around 150 mV. Noticeable, at higher pressure the same improvement can be achieved at higher  $t_{\rm HP}$ , which is a logical consequence of slower gas bubble saturation at higher applied pressure (Figure 2.5D). However, the compression costs also increase with the higher pressure, also when taking into account the larger possible  $t_{\rm HP}$ . When compression costs are included, the best performing pressure swing is between 1-2 bar, with an improvement of -120 mV in cell voltage.

Similar results are obtained at lower current densities, SI 2.5.9. Here, less gas is produced, so higher  $t_{\text{HP}}$  values still result in an improvement of the cell voltage. However the compression costs have a relatively bigger impact, as the power consumption of the electrolyzer goes down, while the compression costs remain unchanged.

Although the pressure swing is effective at 1-2 bar and 200 mA cm<sup>-2</sup>, higher current densities would require even smaller (<5 s)  $t_{\rm HP}$  values, which can cause difficulties from an engineering point of view and would increase the compression costs. Increasing the low pressure and high pressure could be a solution for both problems. At high pressures higher  $t_{\rm HP}$  values are possible and the compression costs scale with gas volume difference, so increasing the low pressure could make the pressure swing economically more attractive. For example, operating a hypothetical pressure swing between 30 and 40 bar could create a large average voltage improvement, while also saving on downstream hydrogen compression (compared to a system with a low pressure of 1 bar).

# MODEL ANALYSIS OF PRESSURE SWING ASSISTED ELECTROLYSIS

To assess the possibilities of pressure swing assisted alkaline electrolysis system, we calculated the change of the average cell voltage under various conditions. A simple analytical model was made and implemented in Python (SI 2.5.11). The compression costs of the pressure swing are included in these calculations. The model uses experimental values of this chapter (e.g.  $R_{\text{Bubbles}}$  and  $V_0$ ).

Figure 2.8A predicts of how much the operating voltage of an electrolyzer can be improved by a 1-2 bar pressure swing. A room temperature electrolyzer (1 M KOH or 6 M KOH) with nickel foam electrodes could benefit significantly (< -0.2 V) from a pressure swing. However, an electrolyzer operating at industrial conditions (6 M KOH and 80 °C) will see limited, (0 to 0.1 V), improvements from a pressure swing. The red regions in Figure 2.8 (>0 V) indicate operating regions where the compression energy costs outweigh the gain in operating voltage. A pressure swing should not be implemented in such a scenario. Figure 2.8B shows that an electrolyzer with perforated plate electrodes will benefit little from a pressure swing. This is in agreement with our experiments, in which the effectiveness of a pressure swing in an electrolyzer with perforated plates is limited (Figure 2.6 and SI 2.5.12).



Figure 2.8: Predicted maximum voltage change for a 1-2 bar pressure swing assisted zero-gap alkaline electrolyzer as a function of current density and electrolyte conductivity. Compression costs of the pressure swing are included. See SI 2.5.11 for the description of the model **A**. An electrolyzer operating with Ni foam electrodes *B*. Ni perforated plate electrodes

The reduction of the cell voltage is similar to other gas bubble removal techniques, like ultrasound [45] or supergravity [41], even after the additional energy costs for a pressure swing are taken into account. Additionally, a pressure swing can be implemented and scaled up relatively easily, as only an expansion tank and solenoid valves need to be installed at the in- and outlet of the electrolyzer. In comparison, ultrasound waves will dampen out and lose strength over larger electrolyzer stacks and supergravity through centrifuges becomes more difficult to implement at large systems. Pressure swing-assisted electrolysis can also easily be combined with other bubble mitigation strategies (i.e. superwetting electrodes or flow-through electrolyzers) to minimize bubble effects.

However, the implementation of a pressure swing on an industrial alkaline electrolysis plant will also bring some difficulties. Large pressure differences, fast-moving valves and pumps increase the amount of hazards in a plant and will require extra maintenance and monitoring. In addition, the pressure swing will also results in a fluctuating voltage (or fluctuating current when operating at constant voltage), which is challenging to supply at a large scale and could damage catalyst surfaces.

While the application of a pressure swing on an industrial electrolyzer might be difficult, it has promise as a testing rig to analyse the effects of gas bubbles in various electrolyzer designs. Gas bubble removal with a pressure swing allows to decouple the effects of gas bubbles from the total ohmic resistance. Furthermore, the technique could also be used for gas bubble removal from porous materials in different systems, such as H<sub>2</sub> generation from borohydrides[53], fouling removal in membrane processes[54] or CO<sub>2</sub> capture with organic redox agents[55]. 2

# **2.4.** CONCLUSIONS

The effects of gas bubbles on the cell voltage in a zero-gap alkaline electrolyzer were investigated with a pressure swing. We demonstrate a pressure swing which removes gas bubbles attached to the electrode in a fast (<1 s) swing between high pressure (2-5 s)bar) and atmospheric pressure. A zero-gap configuration still suffers from gas bubbles, represented by a substantial bubble resistance  $R_{\text{Bubbles}}$ , although the bubble effects are smaller than in a regular gap electrolyzer. R<sub>Bubbles</sub> strongly depends on the electrode geometry; a Ni perforated plate has a much lower bubble resistance (0.3  $\Omega$  cm<sup>2</sup>, 1 M KOH, 30 °C) than a foam electrode (1.8  $\Omega$  cm<sup>2</sup>, 1 M KOH, 30 °C). By investigating the saturation time, it was discovered that the gas bubble volume ( $V_0 = 0.045 \text{ mL cm}^{-2}$ ) is close to the pore volume in foam electrodes (0.048 mL cm<sup>-2</sup>), which means that foam electrodes in a flow-by configuration are almost completely filled with gas bubbles. The timescale for gas saturation is in the second (<5 s) range at 2 bar, the optimal time between two pressure swings  $(t_{\rm HP})$  is around 5 s too. Finally, under industrial conditions (6 M KOH, 80 °C) a pressure swing could reduce the cell voltage by 0.1 V at 1 A cm<sup>-2</sup> for foam electrodes. However, this is mainly because foam electrodes have a very large bubble resistance. In perforated plate electrodes under industrial conditions, the energy gain of a pressure swing is limited because the required compression energy is larger than the voltage gain. We believe that the pressure swing has therefore most value as a gas bubble analysis method at both scientific and industrial scale.

# **2.5. SUPPLEMENTARY INFORMATION**

# **2.5.1. Pressure swing operation scheme**



Figure S2.1: Schematic representation of the operation of the pressure swing

# **2.5.2.** EFFECT OF AN ELECTROLYTE FLUSH

During initial experiments, the effect of flushing a large electrolyte volume through the electrolyzer was tested as a means to remove gas bubbles. In the images below it can be seen that the gas bubble removal is not perfect, even at a flush of 31.5 mL (1.5x electrolyzer volume). Gas bubble removal became more efficient once the pressure variations of the pressure swing were implemented.



Figure S2.2: Images of the electrode before and after an electrolyte flush.

# **2.5.3.** CALCULATION OF NI FOAM PORE VOLUME Ni foam - RCM-Ni4753.005 :

- Thickness: 0.5 mm
- Electrode area: 1 cm<sup>2</sup>
- Porosity: 95.2%
- Volume:  $1 \text{ cm}^2 * 0.05 \text{ cm} = 0.05 \text{ mL}$

Pore volume:  $0.05 \text{ mL cm}^{-2} * 0.952 = 0.0476 \text{ mL cm}^{-2}$ 

conductivity, and that the values converge on 0.41-0.47 cm for foam electrodes.							
Electrode geometry	p (bar)	[KOH] (mol L <sup>-1</sup> )	$\kappa$ (S cm <sup>-1</sup> )	$R_{\text{Bubbles}}$ ( $\Omega \text{ cm}^2$ )	R <sub>Bubbles</sub> *κ (cm)	$V_0$ (cm <sup>3</sup> cm <sup>-2</sup> )	
Foam	2	1	0.23	1.8		0.045	
Foam	3	1	0.23	1.95		0.076	
Foam	4	1	0.23	1.4		0.054	
Foam	5	1	0.23	1.4		0.069	
Foam	2	0.3	0.075	1.9	0.14	0.034	
Foam	2	1	0.23	1.8	0.41	0.045	
Foam	2	2	0.405	1.15	0.47	0.04	
Foam	2	3	0.531	0.78	0.41	0.043	
Foam	2	6	0.685	0.63	0.43	0.043	
Foam [48] (with gap)	4	6	0.685	0.91		N/A	
Perf plate	2	1	0.23	0.3		N/A	

# **2.5.4.** FITTED $R_{\text{Bubbles}}$ AND $V_0$ VALUES

Table S2.1: Fitted  $R_{\text{Bubbles}}$  and  $V_0$  from pressure swing experiments. Electrolyte conductivity is calculated at 30 °C with equations from Gilliam et al.[56]. In the column  $R_{\text{Bubbles}}^*\kappa$  we show that area resistance scales with conductivity, and that the values converge on 0.41-0.47 cm for foam electrodes.

# **2.5.5.** COMPARISON WITH LITERATURE

Bakker & Vermaas[48]:

A value for  $R_{\text{Bubbles}}$  for a regular gap electrolyzer with Ni foam electrodes at 6 M KOH was calculated from Figure 7 of the work of Bakker & Vermaas[48], who also used a pressure swing to remove gas bubbles. Here we assumed that the  $\Delta E_S$  from this work is similar to the  $\Delta E_{\text{Bubbles}}$  that was used in this work. We believe the linear slope in the  $\Delta E_S$  vs current density graph indicates a similar Ohmic relation (and hence an  $R_{\text{Bubbles}}$  can be calculated from this. The trendline in Fig 7 has a slope ( $R_{\text{Bubbles}}$ ) of 0.905  $\Omega$  cm<sup>2</sup>.

De Groot & Vreman[16]:

De Groot and Vreman performed simulations of a zero-gap electrolyzer with a perforated plate electrode, for different gas fractions in the electrode-diaphragm gap ( $Z_1$ ) and in the bulk ( $Z_2$ ). The bubble resistance was calculated from the resistance values from Table 4 of the article (see selected values in Table S2.2). Here we assumed a bulk gas fraction between 0 - 0.3 and a gap gas fraction between 0.6 - 0.999, which is in line with our measurements. The resistance ( $R_0$ ), without diaphragm or gas bubbles can be taken from case A0:

$$R_0 = R - R_{\text{diaphragm}} = 0.021 \,\Omega \,\text{cm}^2 \tag{S2.1}$$

To calculate the effect of gas bubbles ( $R_{\text{Bubbles}}$ ) we assume the following (see Table S2):

$$R_{\text{Bubbles}} = R - R_{\text{diaphragm}} - R_0 \tag{S2.2}$$

At 300 mA cm<sup>-2</sup> we measured a gas fraction of 0.25 (Figure S2.5), and we expect the electrodemembrane gap to be almost completely filled. We therefore expect  $R_{\text{Bubbles}}$  to be between 0.024-0.080  $\Omega$  cm<sup>2</sup> for a perforated plate electrode. The simulations of de Groot and Vreman were done for 30wt% KOH at 80 °C. When we convert the measured  $R_{\text{Bubbles}}$  (0.3  $\Omega$  cm<sup>2</sup>, 1M KOH 30 °C) from our experiments to this conductivity, the resulting  $R_{\text{Bubbles}}$  is 0.051  $\Omega$  cm<sup>2</sup>. This agrees with the simulations of de Groot and Vreman.

Case	$\alpha_1$ (gap)	$\alpha_2$ (bulk)	R <sub>diaphragm</sub>	R	R <sub>Bubbles</sub>
A0	0	0	0.11	0.131	0
A2	0.6	0	0.109	0.145	0.015
A3	0.999	0	0.134	0.194	0.039
A5	0.6	0.3	0.112	0.157	0.024
A6	0.999	0.3	0.135	0.236	0.08

Table S2.2: Selected values taken from the work of de Groot & Vreman [16] (Table 4 of their work), all resistances are in  $\Omega\ cm^2$ 

<u>Kraglund PhD Thesis[50]</u>: A value for  $R_{\text{Bubbles}}$  for a foam electrode was extracted from figure 4.11 from the PhD thesis of Mikkel Kraglund (Figure S2.3). From figure B, the m-PBI resistance can be extracted:  $R_{\text{membrane}} = 0.042 - 0.022 \,\Omega \,\text{cm}^2 \sim 0.020 \,\Omega \,\text{cm}^2$ .  $R_0 = R - R_{\text{membrane}} \sim 0.022 \,\Omega \,\text{cm}^2$ . As there are two perforated plate electrodes, we assumed:

$$R_{\text{Bubbles}}(\text{perf plate}) = 0.5R_0 = 0.011\,\Omega\,\text{cm}^2$$
 (S2.3)

In figure A, the only difference between the red and orange line is that one perforated plate electrode has been swapped with a foam electrode. The specific resistance increased from 0.042 to 0.078  $\Omega$  cm<sup>2</sup>.

$$R_{\text{Bubbles}}(\text{foam}) = 0.078 - 0.042\,\Omega\,\text{cm}^2 + R_{\text{Bubbles}}(\text{perf plate}) = 0.047\,\Omega\,\text{cm}^2 \qquad (S2.4)$$

The foam has a 4.3 times higher  $R_{\text{Bubbles}}$ . Although the dimensions of our electrodes are not the same, the order of magnitude agrees with our measurements



**Fig. 4.11:**  $R_s$  values obtained from equivalent circuit fitting. (a) Obtained values from different types of cells. (b) Identical cells with two different membrane thickness's.

Figure S2.3: Specific resistance values from the work of Kraglund, for a zero gap electroylser with a m-PBI membrane, foam(f) and/or perforated plate (pp) electrodes[50]. T= 80 °C, 24wt% KOH

# **2.5.6.** Photo of the electrodes



Figure S2.4: Photograph of a Ni perforated plate (left) and Ni foam (right) electrode surfaces. Metric ruler for scale

# **2.5.7.** CALCULATION OF THE ENERGY COSTS REQUIRED FOR THE PRESSURE

# SWING

To calculate the additional compression work that the pump has to perform on top of normal operation without a pressure swing, the following assumptions were made:

- Gas fraction of 25% (this is a worst case assumption, see Figure S2.5)
- Pump efficiency of 50%
- · Liquid is incompressible, all compression costs are gas compression
- · Adiabatic process
- Ideal gas



Figure S2.5: Catholyte gas fraction ( $x_{gas}$ ) versus current density at 2 bar pressure on Ni foam electrodes. The gas fraction was measured by operating the cell for 2 min and then closing all the valves around the electrolyzer. The system was drained, electrolyte was weighed and compared to a system operating at 0 mA cm<sup>-2</sup>. All measurements were performed 4 times and an average of the gas volume was taken.

The work for the compression is defined as follows: dW = pdV, where:

$$dV = V_{\text{cell}} x_{gas} \left( \frac{1 \text{ bar}}{p} - 1 \text{ bar} \right)$$
(S2.5)

Where  $V_{\text{cell}}$  is the volume of the electrolyzer and tubing until the back pressure valve (in m<sup>3</sup>),  $x_{\text{gas}}$  is the gas fraction (25%) and p is the high pressure in bar. For these experiments  $V_{\text{cell}}$  is 44 mL, or 44 10<sup>-6</sup> m<sup>3</sup>.

The compression costs are then converted to power:

$$P_{\text{compression}} = dWf = \frac{dW}{t_{\text{HP}} + t_{\text{LP}}} = \frac{dW}{t_{\text{HP}} + 1.5 \text{ s}}$$
(S2.6)

Where *f* is the frequency of the pressure swing, and  $t_{\text{HP}}$  and  $t_{\text{LP}}$  are the high and low pressure time respectively. In all experiments  $t_{\text{LP}}$  was held constant at 1.5 s.

The compression power was converted into an equivalent voltage to be added to  $E_{cell}$  as:

$$E_{\text{compression}} = \frac{P_{\text{compression}}}{I} = \frac{P_{\text{compression}}}{jA}$$
(S2.7)

Where *I* is the current in A, *j* is the current density in A cm<sup>-2</sup> and *A* is the electrode area in cm<sup>2</sup>, which was 40 cm<sup>2</sup> in all experiments.

# 2.5.8. PRESSURE SWING ASSISTED OPERATION AT LARGER PRESSURE DIF-FERENCES



Figure S2.6: Average cell voltage for 1-2, 1-3, 1-4 and 1-5 bar pressure swings for different high pressure times, compared to the average voltage without applying a pressure swing. Note: The change in average cell voltage for the different pressures is likely due to slight movements in the membrane/electrodes in the cell during the cell assembly.





Figure S2.7: Average cell voltage for a 1-2 bar pressure swings at 40, 80 and 200 mA cm<sup>-2</sup>, compared to the average voltage without applying a pressure swing.

### **2.5.10.** CALCULATION OF THE FILLING TIME OF THE ELECTRODES

The filling time of an electrode is the time it takes for the pores of the electrode to be completely filled with hydrogen and oxygen gas bubbles. This is a hypothetical value, were it is assumed that no gas escapes from the electrode pores and the formed hydrogen and oxygen bubbles follow the ideal gas law (i.e. molar volume of 24.9 L mol<sup>-1</sup> gas at 30 °C & atm). The molar volume of the gas is calculated with the ideal gas law:  $V_M = \frac{V}{n} = \frac{RT}{p}$  Here  $V_M$  is the molar volume (mL mol<sup>-1</sup>), *T* is the temperature (K), *p* is the pressure (bar) and *R* is the ideal gas constant (83.14 mL bar K<sup>-1</sup> mol<sup>-1</sup>).

The production rate of hydrogen and oxygen gas are:  $\dot{V}_{gas} = \frac{j}{nF} V_M$  Where  $\dot{V}_{gas}$  is the gas production (mL s<sup>-1</sup>), *j* is the current density (A cm<sup>-2</sup>), *F* is the Faraday constant (96485 C mol<sup>-1</sup>) and *n* is a stoichiometric constant. *n* is 2 for hydrogen gas and 4 for the anode, we assumed *n* to be 3 to find the average fill time over the two electrodes. The filling time is then defined as:  $t_{fill} = \frac{V_{pore}}{V_{gas}}$  where  $t_{fill}$  is the filling time (s) and  $V_{pore}$  is the volume of the pores in the electrode (mL).

The nickel foam from Recemat BV (RCM-Ni4753.005) has a thickness of 0.5 mm and a porosity of 95.2%, resulting in a pore volume of 0.048 mL cm<sup>-2</sup>. At 200 mA cm<sup>-2</sup> and 2.1 bar, the filling time is 4.91 s, which is about 50% of the time it takes to reach a steady state voltage at these conditions. This value of 50% holds up for all measured current densities between 40-300 mA cm<sup>-2</sup>. It is logical

that the actual relaxation time of the voltage is higher, as gas continuously escapes the electrode. This was also observed in videos of the setup, where gas bubbles were observed in the electrolyte at times below  $t_{\text{fill}}$ .

# **2.5.11. PRESSURE SWING MODEL**

Figure 2.8 calculates the improvement to the cell voltage  $E_{\text{red}}$  by applying a pressure swing to our zero-gap electrolyzer.  $E_{\text{red}}$  was calculated by the difference between the voltage reduction by removing gas bubbles  $0.5^*\Delta E_{\text{Bubbles}}$  and the pumping costs required for the pressure swing  $\Delta E_{\text{pump}}$ , the factor 0.5 is because when pressure swing is operated at the saturation time, the average cell voltage is reduced by half of the  $\Delta E_{\text{Bubbles}}$  (Figure S2.8):

$$E_{\rm red} = 0.5\Delta E_{\rm Bubbles} - \Delta E_{\rm pump} \tag{S2.8}$$



Figure S2.8: Assumed cell voltage during the pressure swing operation

 $\Delta E_{\text{Bubbles}}$  is calculated from the current density *j*, the experimentally determined bubble resistance  $R_{\text{Bubbles}}$ , which are 1.8  $\Omega$  cm<sup>2</sup> and 0.3  $\Omega$  cm<sup>2</sup> for Ni foam and perforated plate electrodes respectively (1 M KOH 30 °C) the electrolyte conductivity  $\kappa$  and the conductivity at 1 M KOH and 30 °C ( $\kappa_0 = 0.230$  S cm<sup>-1</sup>):

$$\Delta E_{\text{Bubbles}} = j R_{\text{Bubbles}} \frac{\kappa}{\kappa_0} \tag{S2.9}$$

 $\Delta E_{\text{pump}}$  is calculated by dividing the required pumping power for the pressure swing  $P_{\text{pump}}$  divided by the current *I*, or the current density *j* and the geometric electrode area *A*.

$$\Delta E_{\text{Pump}} = \frac{P_{\text{Pump}}}{I} = \frac{P_{\text{Pump}}}{jA} \tag{S2.10}$$

 $P_{\text{pump}}$  is calculated with the work required for a single pressure swing  $W_{\text{pump}}$  and frequency  $t_{\text{fill}}^{-1}$  (see 2.5.7).

$$P_{\text{Pump}} = \frac{W_{\text{Pump}}}{t_{\text{Fill}}} \tag{S2.11}$$

 $W_{\text{Pump}}$  is calculated with similar to 2.5.4, Here *p* is the high pressure of the pressure swing in Pa,  $y_{\text{gas}}$  is the gas fraction inside the electrolyzer (0.25 taken as conservative value),  $V_{\text{cell}}$  is the liquid volume inside the electrolyzer (44 mL for our system) and  $\eta_{\text{pump}}$  the pump efficiency (50% taken as conservative estimate).

$$W_{\rm Pump} = -\frac{p y_{\rm gas} V_{\rm cell}}{\eta_{\rm Pump}} (\frac{10^5}{p} - 1)$$
 (S2.12)

 $t_{\text{fill}}$  is calculated similar to 2.5.10, where  $V_{\text{pore}}$  is the pore volume in the electrode in m<sup>3</sup> cm<sup>-2</sup>, *j* current density in A cm<sup>-2</sup>,  $n_{\text{O2}}$  is 4, *F* is the Faraday constant, *R* the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), *T* temperature in Kelvin and *p* is the high pressure of the pressure swing in Pa.

$$t_{\text{fill}} = \frac{V_{\text{pore}} n_{\text{O2}} FRT}{jp}$$
(S2.13)

The model was implemented in Python.

# 2.5.12. PRESSURE SWING WITH FOAM VS PERFORATED PLATE ELECTRODES

Figure S2.9 shows the average cell voltage for various  $t_{\rm HP}$  values for an electrolyzer with Ni foam and Ni perforated plate electrodes. The  $R_{\rm Bubbles}$  of foam electrodes make the Ni foam electrode perform worse at all  $t_{\rm HP}$  values. Due to experimental limitations, we did not manage to measure below a  $t_{\rm HP}$  of 10 s. However, it is likely that the trend continues at lower  $t_{\rm HP}$  and that Ni foam electrode will outperform its perforated plate counterpart when bubble effects are mitigated.



Figure S2.9: Average cell voltage for a 1-2 bar pressure swings for comparing a electrolyzer with Ni foam or perforated plate electrodes operating at  $80 \text{ mA cm}^{-2}$ 

# **2.6.** SUPPLEMENTARY VIDEOS



Video S2.10: Video of cathode during a pressure swing. Ni Foam electrode, 1 M KOH, 1-4 bar, 200 mA cm $^{-2}$ . https://www.youtube.com/watch/fWjIUCNVXcU



Video S2.11: Video of anode during a pressure swing. Ni Foam electrode, 1 M KOH, 1-4 bar, 200 mA cm $^{-2}$ . https://www.youtube.com/watch/CgaMQBYNhWk



Video S2.12: High speed video of cathode during a pressure swing. Ni Perforated Plate, 1 M KOH, 1-2 bar, 80 mA cm<sup>-2</sup>.

hhttps://www.youtube.com/watch/7aLzeHfkz1o



Video S2.13: High speed video of anode during a pressure swing. Ni Perforated Plate, 1 M KOH, 1-2 bar, 80 mA  $\rm cm^{-2}.$ 

https://www.youtube.com/watch/gNBlXdT2GO0

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# 3

# QUINOLINIUM-BASED PROBES FOR PH IMAGING USING FLIM



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Spatiotemporal pH imaging, using fluorescence lifetime microscopy (FLIM) is an excellent technique for investigating dynamic (electro)chemical processes. However, probes that are responsive at high pH values are not available. Here we describe the development and application of dedicated pH probes based on the 1-methyl-7-amino-quinolinium fluorophore. The high fluorescence lifetime and quantum yield, the high (photo)stability and the inherent water solubility make the quinolinium fluorophore well suited for the development of FLIM probes. Due to the flexible fluorophore-spacer–receptor architecture, probe lifetime response, at tuneable pH values between 11 and 13, is achieved by deprotonation of the aromatic amine at the quinolinium core. Probe lifetimes are hardly affected by temperature and the presence of most inorganic ions, thus making FLIM imaging highly reliable and convenient. At 0.1 mM probe concentrations, imaging at rates of 3 images per second, at a resolution of 4  $\mu$ m, while measuring pH values up to 12 is achieved. This enables the pH imaging of dynamic electrochemical processes involving chemical reactions and mass transport.

# **3.1. INTRODUCTION**

Imaging chemical and biological systems can give insights into the local mass transport and reaction kinetics. Fluorescent molecular probes are excellent materials for characterizing these dynamic processes[1, 2]. Characteristics of the medium that are probed may be physical in nature, such as measurements of temperature[3–6], pressure[7], mechanical stress[8], solvent mobility[9–11] or solvent polarity[12]. Alternatively, the chemical composition of the medium, such as pH[13–16], the concentration of ions[17, 18] or more complex chemical species[19–21] can be monitored. A distinct advantage of fluorescent probes is their inherently low detection threshold. Fluorescence can be detected at very low probe concentrations, in principle down to the single molecule, but routinely in the micromolar range (10<sup>-6</sup> M). Because fluorescent probes can be localised by microscopic techniques and fluorescence can be monitored in real time, the use of fluorescent probes enables *spatiotemporal* probing.

In order to detect chemical species, the fluorescence of probe molecules should be influenced by interaction with analytes. In most cases this probe-analyte interaction is a reversible binding event. The most convenient and flexible probe architecture is the modular fluorophore-spacer-receptor configuration[22], in which a receptor is attached to a fluorophore by a flexible spacer, see Figure 3.1. Upon binding the analyte to the receptor, the fluorophore emission is altered and the most commonly encountered fluorescence response is a change in emission intensity. In most cases intensity changes are induced by changing the non-radiative decay rate of the excited state  $k_{nr}$ , as described by Equations 3.1 and 3.2. In these equations,  $k_F$  and  $k_{nr}$  are the rate constants for fluorescence and non-radiative decay, respectively, and  $\Phi_F$  and  $\tau_F$  are the quantum yield and the lifetime of fluorescence. Equations 3.1 and 3.2 clearly express that if the binding event only changes  $k_{nr}$ , which is generally the case for fluorophore-spacer-receptor probes,  $\Phi_F$  and  $\tau_F$  will be proportional.

$$\Phi_{\rm F} = \frac{k_{\rm F}}{k_{\rm F} + k_{\rm nr}} \tag{3.1}$$

$$\tau_{\rm F} = \frac{1}{k_{\rm F} + k_{\rm nr}} \tag{3.2}$$

Although an altered fluorescence intensity provides information about the local analyte concentration, this is not the most desired probe response, because fluorescence intensity also changes with probe concentration, which may be problematic in case of an uneven probe distribution. Also, the recorded probe intensity is influenced by other factors such as fluctuations in lamp intensity, photobleaching of the probe and light scattering in the medium. Probes that respond to environmental changes by emission wavelength shifts, so-called ratiometric probes, are more desirable. The fluorescence response of such probes is more robust and reliable as the probe response no longer depends on the probe concentration and excitation light intensity and is less sensitive to scattering of the medium. For that reason, ratiometric probes are often referred to as "self-referencing" probes. Unfortunately, ratiometric probes are far less common than intensity probes, mainly because emission wavelength shifts are generally accompanied by severe changes in emission intensity[23–26]. Technical advancements in recent years have made fluorescence lifetime measurement an affordable, highly accessible and user-friendly technique[27, 28]. Lifetime probes are self-referencing because lifetimes are independent of probe concentration, excitation light intensity and hardly influenced by scattering. Using fluorescence lifetime imaging microscopy (FLIM), spatiotemporal probing at high spatial and temporal resolution has become an established technique.

Fluorescence intensity changes result in changes to the fluorescence lifetime for most probes, as expressed in Equations 3.1 and 3.2. Therefore, intensity sensitive probes can be used as self-referencing fluorescence lifetime probes as well. Probe requirements for lifetime probes, however, are different from those of intensity probes. The main requirements for intensity probes are high fluorescence quantum yields in the "on-state" and low quantum yields in the "off-state", resulting in large fluorescence enhancements, Fl.E  $= I_{\rm on}/I_{\rm off}$ . For FLIM application, probes with high fluorescence quantum yields, long lifetimes[29, 30] and modest changes in emission intensity are required. Generally, the lifetimes and fluorescence quantum yield of probe molecules, in their bound and unbound state, are proportional, providing that the analyte binding does not severely affect the intrinsic photophysical properties of the fluorophore. For fluorophore-spacer-receptor probes  $k_{\rm F}$  will not change significantly because the binding event does not take place directly at the fluorophore. At analyte concentrations around the dissociation constant of the receptor unit, mixtures of bound and unbound probes are formed resulting in dual lifetime emissions. While the emission intensity scales linear with the (un)bound probe concentration, the average lifetime in this probe mixture, as given by equations 3.3 and 3.4, does not. The fluorescence lifetime is dominated by the strongly fluorescent and long-lived species, as expressed by equation 3.4[28].

$$I_{\rm F}(t) = \sum C_{\rm i} \exp\left(\frac{t}{\tau_{\rm i}}\right) \tag{3.3}$$

$$\tau_{\rm avg} = \frac{\sum C_i \tau_i}{\sum C_i} \tag{3.4}$$

In equations 3.3 and 3.4,  $\tau_i$  is the fluorescence lifetime of species i,  $\tau_{avg}$  is the average lifetime of the different probe species and the term  $C_i$  is called the pre-exponential factor, which represents the magnitude of the species i in the fluorescence decay profile. It is assumed that the pre- exponential factor is the product of concentration and fluorescence quantum yield and therefore the lifetime response will deviate from the intensity response, in particular when analyte binding induces strong changes in fluorescence quantum yields.

The prospect of using FLIM for *spatiotemporal* probing, i.e. real time monitoring of complex processes in three-dimensional space, has been exploited for examining biological processes, using probes that are sensitive to pH, other relevant chemical species such as reactive oxygen species ( $R_{ox}$ )[20], or temperature[5]. In recent years FLIM probes have been developed aimed at probing pH, temperatures and chemical species at biologically relevant conditions. For pH probing, lifetime probes that monitor pH changes in mildly acidic and neutral media, in the pH domain between 5 and 8, are commercially available[31].

Recently, real-time monitoring of complex systems in two dimensions using FLIM has also been employed for non-biological processes. Using conventional probes, pH gradients in electrochemical processes[32] and flow through porous catalysts have been monitored[33]. In our current research we are investigating electrochemical processes that are relevant for the coming energy transition, such as electrochemical water splitting and  $CO_2$  reduction. The electrodes in  $CO_2$  reduction typically operate at a high pH and produce or consume  $OH^-$  ions, which results in pH changes at moderately high pH values[34]. In order to study these processes, fluorescence lifetime probes with tune-able properties and sensitivities outside the biological constraints, notably for high pH values, are required.

In previous research we have developed "switch on/switch off" pH probes fluorescent probes based on the 1-methyl-7-amino-quinolinium fluorophore.[14, 35] In addition, ratiometric mobility probes for monitoring physical ageing[36] as well as determining crystallization and glass transition temperatures[37] in amorphous and semicrystalline polymers were developed. The 1-methyl-7-amino-quinolinium fluorophore has (photo) physical properties that are highly suitable for developing lifetime probes for FLIM applications. The fluorophore has a high fluorescence quantum yield in the 0.7-0.8 range and fluorescence lifetimes are in the 12-13 ns range, which is well above the 4 ns lifetime of common fluorophores[33]. On top of that, this fluorophore is inherently water soluble and highly photo stable. Most importantly, using the "fluorophore-spacerreceptor" configuration the pH range in which the probes are sensitive, and the extent of fluorescence quenching are easily tuned by systematic variation of the spacer-receptor units that are attached to this fluorophore.

In this research we will demonstrate that "fluorophore-spacer-receptor" probes based on 1-methyl-7-amino-quinolinium are excellent materials for FLIM probing. Fluorescence lifetimes of these probes are pH sensitive and easily tuned in the pH window between 5.5 and 13. FLIM measurements were demonstrated at 3 Hz with 4  $\mu$ m resolution using a 0.1 mM probe concentration using default settings. Model measurements demonstrate that pH changes due to reactions and mass transfer are visualised accurately and in detail by FLIM measurements.

# **3.2.** Results and discussion

# **3.2.1.** PROBE DESIGN AND SYNTHESIS

The general fluorescence behaviour and the molecular architecture of 7-amino-1methyl quinolinium-based pH probes with a spacer-receptor moiety attached at the 7position is depicted in Figure 3.1. At low pH values, the appended amine receptor is protonated and the probe,  $H_2Q^{2+}$  in Figure 3.1, is highly fluorescent with fluorescence quantum yields  $\Phi_F$  around 0.6-0.8 and fluorescence lifetimes in the 12-13 ns domain. Upon deprotonation of the receptor,  $HQ^+$  is formed and quenching by the amino functionality due to photoinduced electron transfer (PET) occurs[22]. Both the fluorescence quantum yield and lifetime decrease. The pH value at which this transition takes place,  $pK_{A1^*}$ , depends on the excited state acidity of the protonated amine receptor, which depends on the substituents at the amino functionality ( $R_1$  and  $R_2$ ) and the length of the spacer between the electron deficient fluorophore and the receptor unit, see Figure 3.1.



Figure 3.1: General emission intensity versus pH behaviour of quinolinium probes. Values used for constructing this graph are:  $pK_{A1*} = 5$ , Fl.E = 2 and  $pK_{A2*} = 11.5$ .

In a previous contribution, we have reported  $pK_{A1^*}$  values between 6 and 10,[14] but with appropriate modifications of the molecular structure, pK<sub>A1\*</sub> values outside that range can be obtained in a straightforward fashion. The extent of quenching, quantified by the fluorescence enhancement  $Fl.E = I_{on}/I_{off}$ , is mainly determined by the length of the spacer between the fluorophore and the receptor. The shorter the spacer, the stronger the quenching upon deprotonation is. It should be noted that changes in absorption are determined by the ground state dissociation constant  $pK_A$ , while changes in fluorescence depend on the excited state dissociation constant pK<sub>A\*</sub>, providing that equilibrium in the protonation reaction is achieved during the excited state lifetime. For fluorophore-spacer-receptor probes, differences between pK<sub>A</sub> and pK<sub>A\*</sub> values are small. Finally, at higher pH values, deprotonation of the aromatic amino proton at the quinolinium takes place and  $\mathbf{Q}$ , a non-fluorescent species, is formed. This process has an apparent dissociation constant  $pK_{A2^*}$  around  $11[38]^1$ . Ground state deprotonation is not observed for this process, not even at pH values as high as 14, which indicates that only the excited state of  $\mathbf{Q}$  is acidic. Similar excited state proton transfer processes (ESPT) have been reported for related compounds such as the "superacids" 6-,7- and 8-hydroxyquinoline and 6-,7- and 8-aminoquinoline compounds[39]. The large differences in ground state and excited state dissociation constants observed for these com-

<sup>&</sup>lt;sup>1</sup>The reported "apparent" pK<sub>A2\*</sub> values are measured from fluorescence intensity, assuming equilibration prior to fluorescence, which is not necessarily the case. Correct pK<sub>A2\*</sub> values will be lower than the reported "apparent" pK<sub>A2\*</sub> values, see[38]

pounds is not surprising because now the receptor is part of the fluorophore[40], which undergoes (partial) transfer of the positive charge from the quinolinium nitrogen to the amino nitrogen upon excitation.

For lifetime probing, in contrast to intensity probing, modest decreases in intensity upon receptor deprotonation are preferred. This requirement translates into the use of longer spacers (n = 3,4). The full intensity quenching caused by deprotonation at the aromatic amine at high pH values around pH = 11-12, will result in lifetime changes as well. Although full intensity quenching is often not accompanied by lifetime changes[41], decreases in lifetime are expected because deprotonation takes place in the excited state by ESPT, as illustrated by Figure S3.10. This is explained in more detail in the Supporting Information (3.5.2).

Probe molecules **2a-2e**, depicted in Figure 3.2 have been selected for further investigation. Probes **2b** and **2c** have modest 4 fold decreases in emission intensity with markedly different excited state dissociation constants  $pK_{A1^*}$  for the receptor deprotonation of 9.4 and 6.5, respectively. The fluorescence lifetimes change with a factor 3-4 from 12.7 to 3.5 ns upon this deprotonation. The final deprotonation of the aromatic amine has a  $pK_{A2^*}$  value around 12.2 and results in full quenching of the fluorescence. Probe **2a** has a strong 80-fold decrease in emission with a  $pK_{A1^*}$  value of 7.9 and due to this large quenching **2a** is not expected to be a useful lifetime probe. Probes **2d** and **2e** do not have spacer-amino receptors attached to the quinolinium core and fluorescence quenching takes place by deprotonation of the equinolinium amine only. For this process a lower  $pK_{A2^*}$  value is expected for probe **2d** because the ethyl trimethyl ammonium substituent at the aromatic amine in **2d** is more electron withdrawing than the hexyl substituent in compound **2e**. Photophysical properties of probes **2a-2e**, obtained from this work and reference [14], are listed in Table 3.1.

Probe	2a	2b	2c	2d	2e
pK <sub>A1*</sub> (I)	$7.9^{b}$	$9.4^{b}$	$6.5^{b}$	-	-
pK <sub>A1*</sub> (t)	9.3 <sup>b</sup>	$9.7^{b}$	$6.7^{b}$	-	-
pK <sub>A2*</sub> (I)	-	$12.2^{b}$	$12.2^{b}$	$11.3^{b}$	$11.7^{b}$
pK <sub>A2*</sub> (t)	-	$12.4^{b}$	$12.4^{b}$	$11.5^{b}$	$11.9^{b}$
$\Phi_{\text{F-on}}$	0.85 <sup><i>a</i></sup>	0.78 <sup><i>a</i></sup>	0.74 <sup><i>a</i></sup>	0.82 <sup><i>a</i></sup>	$0.59^{b}$
$\tau_{\text{F-on}}$ (ns)	$13.0^{b}$	$12.6^{b}$	$12.7^{b}$	$13.0^{b}$	$11.5^{b}$
$I_{\rm on}/I_{\rm off}$	$80^b$	$4.1^{b}$	$4.2^{b}$	-	-
$\tau_{\rm on}/\tau_{\rm off}$	-	$4.0^b$	$3.7^{b}$	-	-
$\lambda_{\max}^{abs}$ (nm) <sup>c</sup>	$401^{b}$	$410^{b}$	$410^b$	$402^{b}$	$418^{b}$
$\lambda_{\max}^{emi}$ (nm) <sup>c</sup>	486 <sup>b</sup>	$496^{b}$	$494^b$	$484^{b}$	$503^{b}$

Table 3.1: Photophysical data of probes 2a-2e, from previous work and obtained in this work.

*a*: Taken from [14] *b*: This work. *c*: Maximum absorption and emission wavelength for the quinolinium in protonated form. Full absorption and emission spectra can be found in Figure S3.11 and S3.12 respectively

# 3.2.2. SYNTHESIS

The fluorescent quinolinium probes **2a-2e** were synthesised by reacting primary amines with 7-fluoro-1-methylquinolinium iodide **1**[42] by a nucleophilic aromatic substitution reaction, as depicted in Figure 3.2. Probes **2a**, **2c** and **2e** were obtained by reacting 1 with a small excess of amine and were isolated in high yields after crystallisation from the reaction mixtures. Probe **2b** was obtained by a similar procedure, using a 10-fold excess of diamine, in 84% yield. Finally probe **2d** was obtained in 64% yield by alkylation of compound **2a** with methyl iodide in methanol at room temperature.



Figure 3.2: Molecular structure and synthesis of probes 2a-2e.

# **3.2.3.** Photo physical probe characterisation

The fluorescence emission intensities of probes **2a-2e**, as a function of pH, are plotted in Figure 3.3. The data points in Figure 3.3 are the experimental data points, the curves have been obtained using Equation 3.5 that describes the probe composition in the excited state, as a function of pH.

$$\Phi_{\rm F} = \left(\Phi_{\rm F}({\rm H}_2{\rm Q}^{2+}) - \Phi_{\rm F}({\rm H}{\rm Q}^+)\right) \frac{10^{p{\rm K}_{{\rm A}1^*} - p{\rm H}}}{1 + 10^{p{\rm K}_{{\rm A}1^*} - p{\rm H}}} + \Phi_{\rm F}({\rm H}{\rm Q}^+) \frac{10^{p{\rm K}_{{\rm A}2^*} - p{\rm H}}}{1 + 10^{p{\rm K}_{{\rm A}2^*} - p{\rm H}}} \tag{3.5}$$

In Equation 3.5,  $H_2Q^{2+}$ ,  $HQ^+$  and Q are the protonated quinolinium probe, the quinolinium probe and the deprotonated probe, respectively, as depicted in Figure 3.1.  $pK_{A1^*}$ and  $pK_{A2^*}$  are the excited state dissociation constants of the  $H_2Q^{2+}/HQ^+$  and  $HQ^+/Q$ equilibria, respectively.

From Figure 3.3,  $pK_{A1^*}$  values of 7.9, 9.4 and 6.5 are determined for probes **2a**, **2b** and **2c** along with fluorescence enhancements of 80, 4.1 and 4.2, respectively. These values in good agreement with previous work[14]. For probes **2b** and **2c**, an identical  $pK_{A2^*}$  value of 12.2 was determined. Probes **2d** and **2e** do not have amine receptors appended to the quinolinium ions, so only  $pK_{A2^*}$  values of 11.3 and 11.7 were observed. These  $pK_{A2^*}$  values correlate very well with the electron donating ability of the spacerreceptor unit attached to the aromatic amine at the quinolinium moiety. For probe **2d** the strongly electron deficient ethyl trimethylammonium unit induces the lowest  $pK_{A2^*}$  value, whereas the electron-rich amine appended propyl units in probes **2b** and **2c** induce the highest  $pK_{A2^*}$  values in these compounds.



Figure 3.3: Fluorescence intensity vs pH for probes **2a-2e** in a 0.1 mM phosphate buffer. Curves connecting the data points were obtained by using Equation 3.5 or S3.1

Surprisingly, decreases in emission intensity around neutral pH values were observed for compounds **2b**, **2d** and **2e**, with apparent  $pK_{A^*}$  values close to 7.1. For compound **2b** and **2e** decreases in emission intensity are small, 3 and 2%, respectively, but for compound **2d**, the decrease in intensity is a more substantial 12%. We found that the origin of this decreased emission intensity is HPO<sub>4</sub><sup>-2</sup> that is formed in the 10<sup>-4</sup> M phosphate buffer around pH = 7.43. Similar decreases in intensity around pH 7 have been reported for phenol appended DAOTA dyes in phosphate buffers as well[30, 43]. It was noted that this quenching increases if more concentrated buffer solutions are used, see Figures S3.1, S3.2 and S3.3. We assume that is due to hydrogen phosphate binding and that the dicationic probe **2d** has the best geometry for HPO<sub>4</sub><sup>-2</sup> binding. The strong quenching of probe **2d** to HPO<sub>4</sub><sup>-2</sup> could be interesting in the future for developing a HPO<sub>4</sub><sup>-2</sup> concentration probe, similar to anthrylpolyamines reported previously[44]. Finally, the phosphate quenching has been incorporated in Equations S3.1 and S3.5.

The fluorescence lifetime of probes **2a-2e** as a function of pH is depicted in Figure 3.4, while normalised lifetimes versus pH plots are presented in Figure S3.4. At low pH values all probes exhibit lifetimes between 11.5 and 13.1 ns and these values are proportional to the fluorescence quantum yields  $\Phi_F$  of these probes. Changes in lifetimes due to deprotonation of a spacer-bound amine receptor occurs for probes **2a**, **2b** and **2c** only. For probes **2b** and **2c**, by fitting the experimental data using Eq S3.4 (see 3.5.4) pK<sub>A1\*</sub> values of 9.7 and 6.7 were determined from lifetime measurements. These values were 0.2-0.3 units higher than those determined by intensity measurements. This "delayed" response in lifetime was anticipated, because mixtures of  $H_2Q^{2+}$  and  $HQ^+$  are present in the solution, at pH values of pK<sub>A1\*</sub> ± 1, for which the emission is dominated by the strongly emitting, long-lived  $H_2Q^{2+}$ . For probe **2a**, due to the 80-fold quenching upon deprotonation, this effect is most pronounced and the pK<sub>A1\*</sub> measured in lifetime is 9.3; a 1.4 shift compared with the intensity measurements.

For probes **2b-2e**, lifetimes further decrease due to deprotonation of the aromatic amine proton. For probes **2d** and **2e**, whose fluorescence lifetime is not affected below pH 10, this decrease in lifetime is most pronounced. The  $pK_{A2^*}$  values measured in

lifetime are slightly higher than those measured in intensity by a value of 0.2. It should also be noted that, due to the low fluorescence intensity and short lifetimes, lifetimes reported at high pH have limited accuracy.



Figure 3.4: Fluorescence lifetime vs pH for probes **2a-2e** in a 0.1 mM Phosphate buffer. Curves connecting the data points were obtained by using Equation S5 or S6. Error bars, as included in Figures 3.5, 3.5, are not included for better readability.

In Figure 3.5, the normalised fluorescence intensities and lifetimes as a function of pH for probes **2b** and **2c** are depicted, along with the curve fitting based on Equations 3.5 and S3.4. From Figure 3.5 it is clear that the major differences between emission intensity and lifetime curves are that  $pK_{A^*}$  values are right-shifted for the lifetime measurements and that the decreases in lifetime upon deprotonation at higher pH values are smaller than those measured in intensity.



Figure 3.5: Relative intensity and lifetime vs pH of probe **2b** (left) and probe **2c** (right) in water containing 0.1 mM phospate buffer. The curves around the data points are generated using Equation 3.5, S3.1 or S3.4. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.6 for more information.

In Figure 3.6, the normalised fluorescence intensities and lifetimes as a function of pH for probes **2a** and **2e** are depicted, along with the curve fitting based on Equation 3.5. From Figure 3.6 it is visible that for probe **2a**, the lifetime responds to pH changes at much higher pH values at which the probe emission is very low. This is because the probe exhibits a 80-fold intensity decrease around pH = 8. This is so because above pH = 8 (pK<sub>A1</sub>\*) the lifetime is dominated by the strong emission of the protonated probe. For that reason, probes with high fluorescence enhancement, like probe **2a**, are not suitable as lifetime probes. Probe **2e**, responds to pH changes only at very high values due to deprotonation of the aromatic quinolinium proton. Intensity and lifetime of probe **2e** does not respond to hydrophosphate quenching and that the pK<sub>A2</sub>\* in lifetime has increased by a modest 0.2. At high pH values between 11 and 12, N7-alkylated quinolinium probes like **2e** are very sensitive lifetime probes. A similar behaviour is observed for probe **2d**, see Figure S3.5.



Figure 3.6: Relative intensity and lifetime vs pH of probe **2a** (left) and probe **2e** (right) in water containing 0.1 mM phospate buffer. The curves around the data points are generated using Equation 3.5, S3.1 or S3.4. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.6 for more information.

To be useful as pH probes, the probe lifetime should not be influenced by changes in temperature and common ions, such as Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, that we expect to be present in the sample. Previous experiments with 7-ethylamino-1-methylquinolinium iodide[14], the ethyl analogue of probe **2e**, revealed that the probe intensity was insensitive to Cl<sup>-</sup> and Br<sup>-</sup> ions. In contrast, I<sup>-</sup> and OH<sup>-</sup> ions induced quenching due to photo induced electron transfer (PET) and deprotonation of the aromatic amine, respectively. Similar sensitivities are expected for fluorescence lifetimes. The fluorescence lifetimes of probes **2b**, **2d** and **2e** were investigated as a function of the temperature and the concentration of phosphate and sulphate ions. As depicted in Figures 3.7, S3.6 and S3.7, the fluorescence lifetime decreases upon increasing the temperature, with a gradient of 0.05-0.06 ns/°C. As mentioned earlier, hydrogen phosphate ions (HPO<sub>4</sub><sup>2-</sup>) reduce both intensity and lifetime, but at concentrations below 0.1 mM, the effect is negligible for all probes in lifetime measurements and hardly visible in intensity measurements, with the notable exception of probe **2d**, see Figures S3.1-S3.3 and S3.8. The lifetime response of probe **2d** to the sulphate concentration is shown in Figure S3.9. When the sulphate concentration is increased from  $10^{-4}$  to  $10^{-1}$  M, lifetimes between 13.3 ns to 13.6 ns were recorded. This happens both at a pH of 7 and 3.5. These changes fall well within the standard deviation of the FLIM measurements. Hence we can say that pH probing is unaffected by sulphates.



Figure 3.7: Fluorescence lifetime  $\tau_F$  vs temperature of probe 2e in demineralised water. The lifetime vs temperature slope is -0.057 ns/°C

# **3.2.4.** Spatiotemporal pH imaging in aqueous environment

The large pH range of the quinolinium probes enables spatiotemporal pH probing in various pH domains. To demonstrate the possibilities of the quinolinium probes, we have performed two experiments with **2b**. We probed the pH in the vicinity of a CO<sub>2</sub> bubble, which dissolves in the surrounding alkaline medium and monitored the diffusion of Ba(OH)<sub>2</sub> from a small paper bag into the surrounding liquid. The FLIM setup allowed pH imaging using a 0.1 mM probe solution at a rate of up to 3 images per second and at a pixel size of 4 µm.

The dissolution of gaseous  $CO_2$  in an alkaline medium decreases the pH value by forming carbonate ions ( $CO_2 + 2OH^- \leftrightarrow CO_3^{2^-} + H_2O$ ). This phenomenon is also applied when capturing  $CO_2$  from the air[45] or from post-combustion gas streams[46]. Spatiotemporal monitoring the pH during such processes could help to gain insights in the mass transport in these processes. Figure 3.8 shows a bubble of  $CO_2$  gas which is pumped through a needle in a 0.01 M KOH solution. A higher fluorescence intensity can clearly be seen around the bubble on the intensity plot (Figure 3.8B). This is caused by the high fluorescence emission of the dye at lower pH, which is a result of  $CO_2$  dissolving and creating a locally more acidic environment close to the bubble. While the intensity images are highly dependent on dye concentration, excitation intensity and light scattering, the fluorescence lifetime image (Figure 3.8C) allows us to directly measure and visualize the local pH around the  $CO_2$  bubble. Interestingly, both intensity and lifetime measurements show that the radial symmetry that one would expect for  $CO_2$  dissolution is not observed in this experiment: a lower pH is observed at the left top of the gas



bubble, indicating advection in this direction.

Figure 3.8: **A.** Schematic representation of the experiment: A bubble of  $CO_2$  pumped in an alkaline (0.01 M KOH,  $10^{-4}$  M **2b**) solution. **B.** Light intensity image. **C.** Fluorescence lifetime image, calculated from the phase shift from the reference. **D.** pH image, lifetime image was converted using the lifetime pH curve from Figure 3.4. See section 3.6 for the video of this process.

To show that the probe works also in cases with low bulk pH and high surface pH, we injected dye solution ( $0.2 \text{ M K}_2\text{SO}_4$ ,  $10^{-4} \text{ M }2b$ ) on top of a paper bag filled with Ba(OH)<sub>2</sub> and monitored the diffusion of the OH<sup>-</sup> ions into the solution (Figure 3.9). The lifetime and pH images in Figure 3.9C/D show a complex mixing behaviour resulting from the liquid being injected into the cuvette and the beginning of the formation of an alkaline layer above the paper bag.

The additional strength of the FLIM technique, in combination with the quinolinium probes, are demonstrated by the pH videos in section 3.6. These videos allow great insights in the mixing dynamics in these systems. For example, when the  $CO_2$  bubble emerges from the tube one can clearly see a swirl with a decreased pH forming above the bubble. Similar swirls were formed in repeat experiments and would be difficult to model. Also in the Ba(OH)<sub>2</sub> diffusion experiment one can see complex mixing behaviour when the liquid is pumped into the cuvette, and the resulting inhomogeneities in the pH in the electrolyte above the paper bag. The fast imaging of the FLIM camera, combined with the large and tuneable range in pH, facilitates mapping of mass transport in elec-



trochemical flow cells, such as flow batteries or CO<sub>2</sub> electrolyzers.

Figure 3.9: **A.** Schematic representation of the experiment: Cuvette with a small paper bag filled with  $Ba(OH)_2$  powder, on which electrolyte (0.2 M K<sub>2</sub>SO<sub>4</sub>,  $10^{-4}$  M **2b**) is added using a 5 mL syringe. **B.** Light intensity image. **C.** Fluorescence lifetime image, calculated from the phase shift from the reference. **D.** pH image, lifetime image was converted using the lifetime pH curve from Figure 3.4. See section 3.6 for the video of this process.

It should be noted that 1-methyl-7-aminoquinolinium-based fluorescent pH probes allowed for accurate pH resolution, as lifetime changes are large (1-10 ns), much larger than the standard deviation in the measurements (0.5-1 ns). The intensity of the quinolinium dyes remained unchanged for long (~1 hour) experiments, which indicates a high photostability. Commercial FLIM pH probes, like BCECF[31], SNARF-5F[31] and Fluorescein[47], on the other hand, have much smaller lifetime change of around 0.5-1 ns and exhibit significant decreases in fluorescence intensity due to photo bleaching under standard irradiation conditions. These commercial dyes did not yield accurate and dynamic pH information in our setup and were not sensitive at high pH values. Finally, it should be noted from Figures 3.8 and 3.9 that the images taken from intensity measurements, Figures 3.8B and 3.9B, are "contaminated" with dark spots and other artefacts (vertical lines in 3.9B) that are not present in the lifetime and pH images.

# **3.3.** CONCLUSIONS

In this work we have demonstrated that 1-methyl-7-aminoquinolinium-based fluorescent pH probes are excellent spatiotemporal pH probes by fluorescence lifetime imaging (FLIM). These fluorescent probes are inherently water soluble and highly photo stable, have high inherent lifetimes (11.5-13 ns) and have limited sensitivity to temperature and common ions present in the aqueous media that we investigated. Preliminary experiments have demonstrated that dynamic processes involving chemical reactions and mass transfer, can be imaged with a spatial resolution of 4  $\mu$ m at a rate of 3 images per second using 0.1 mM probe concentrations.

Due to the modular design, sensitivities of the probe molecules are easily tuned in a pH range between 5 and 11 by attaching spacer-receptor units to the quinolinium core. An additional tuneable regime around pH 11-13 is available by deprotonating the quinolinium fluorophore. Notably the tuneable sensitivity at high pH values is unprecedented for FLIM probes and makes the quinolinium probes excellent candidates for investigating local pH effects in complex (electro)chemical reaction systems.

Finally, it was demonstrated that the pH-dependence of fluorescence lifetimes and fluorescence intensities, apart from a 0.2 pH unit shift to higher values, were very similar, for probes with modest fluorescence enhancements. Therefore, data available from pH-dependent fluorescence intensity measurements are useful input for the development of FLIM probes.

# **3.4.** METHODS

# **PROBE SYNTHESIS AND CHARACTERISATION**

Probes **2a-2d**, were synthesised according to the procedures described in reference [14]. The synthesis and characterisation of probe **2e** is described in the Supporting Info (3.5.5).

# ABSORPTION SPECTRUM CHARACTERIZATION

The absorption spectra of the Quinolinium dyes were taken on a Perkin Elmer Lambda 40 by dissolving  $10^{-4}$  M dye in a  $10^{-4}$  M phosphate buffer solution in polystyrene cuvettes, one solution acidified to pH 2.5 by addition of 0.025 M HCl and one to pH 13 by addition of 0.1 M KOH.

## FLUORESCENCE INTENSITY MEASUREMENTS

The fluorescence intensity/pH curves were made using 200 mL of stirred buffered dye solution,  $10^{-4}$  M phosphoric acid, and quinolinium was added until the absorbance was 0.12 in a standard quartz cuvette. A few drops of 37% HCl were added at the start to reduce the pH to 2-3. The pH was increased by adding KOH. The pH was monitored using a 913 pH Meter from Metrohm. The fluorescence spectra were taken on a Jobin Yvon-Spex Fluorolog 3-11 spectrofluorimeter and the fluorescence intensity was measured at the wavelength of the emission maximum at low pH ( $\lambda_{max}$ ).

# FLUORESCENCE LIFETIME MEASUREMENTS

The lifetime/pH curves were made using 200 mL of stirred buffered dye solution  $(10^{-4} \text{ M quinolinium and } 10^{-4} \text{ M Phosphoric acid})$ . A few drops of HCl were added at
the start to reduce the pH to 2-3. The pH was increased by adding KOH solution manually with a pipette. The pH was monitored using a 913 pH Meter from Metrohm (pH accuracy of  $\pm 0.003$  pH) and samples were taken and stored in polystyrene cuvettes. We made sure the total volume increase was less than 25% to prevent significant dilution of the dye.

The lifetimes were measured with a Toggel FLIM camera from Lambert instruments (frequency-domain), in combination with a X-Light V2 spinning disk confocal unit from CrestOptics (see 3.5.6). The solutions were excited by a 405 nm modulated laser (Omicron LuxX+ 405-300). The FLIM camera and confocal disk unit were connected to a Zeiss Axiovert 200m microscope with a 5x objective, in which a cuvette can be mounted. The fluorescence from the samples are filtered by a long-pass filter with a cutoff at 420 nm. We used a strongly buffered solution of **2b** (pH = 8) as a fluorescence lifetime reference ( $\tau_{\phi} = 10$  ns,  $\tau_{\phi}$  is the fluorescence lifetime calculated by phase shift) in all experiments. All reported lifetimes are calculated with the frequency method ( $\tau_{\phi}$ ) in the LIFA software from Lambert instruments. Photographs of the setup and full instrument settings are shown in the supplementary information. To check the validity of the lifetime measurement method, the lifetimes were also measured on a Lifespec-PS from Edinburgh instruments (time-domain). See 3.5.6 for more information.

#### FLIM DEMONSTRATION EXPERIMENTS

The FLIM demonstration experiments were performed on the same setup as the lifetime measurements. The CO<sub>2</sub> bubble dissolution experiment was done in a polystyrene cuvette (1x1x3.5 cm), CO<sub>2</sub> gas was flown through a small steel needle into the electrolyte, which consisted of 0.01 M KOH and  $10^{-4}$  M **2b**. The Ba(OH)<sub>2</sub> diffusion experiment was performed by carefully adding an electrolyte of 0.2 M K<sub>2</sub>SO<sub>4</sub> and  $10^{-4}$  M of dye **2b** into a cuvette which had a small paper bag filled with Ba(OH)<sub>2</sub> powder.

#### **3.5. SUPPLEMENTARY INFORMATION**

#### **3.5.1.** EFFECT OF PHOSPHATE BUFFER, SULPHATES AND TEMPERATURE

Quenching of fluorescence intensity and lifetime is observed at high concentration phosphate buffers due to the formation of hydrogen phosphate dianions (HPO<sub>4</sub><sup>2-</sup>) at increasing pH. Phosphorous acid has 3 dissociation constants with pK<sub>A</sub> values of pK<sub>A1</sub> = 2.2, pK<sub>A2</sub> = 7.2 and pK<sub>A3</sub> = 12.4, respectively. Therefore the hydrogen phosphate quenching process will be observed when HPO<sub>4</sub><sup>2-</sup> becomes present in the solution, so pH values around 6.2-7.2. For describing fluorescence intensity versus pH plots of probes **2a-2e**, Equation 3.5 is appended to form equation S3.1:

$$\begin{split} \Phi_{\rm F} &= \left( \Phi_{\rm F}({\rm H}_{2}{\rm Q}^{2+})_{{\rm H}_{2}{\rm PO}_{4}^{-}} - \Phi_{\rm F}({\rm H}_{2}{\rm Q}^{2+})_{{\rm HPO}_{4}^{2-}} \right) \frac{10^{({\rm pK}_{\rm A2} - {\rm pH})}}{1 + 10^{({\rm pK}_{\rm A2} - {\rm pH})}} + \\ & \left( \Phi_{\rm F}({\rm H}_{2}{\rm Q}^{2+})_{{\rm HPO}_{4}^{2-}} - \Phi_{\rm F}({\rm HQ}^{+})_{{\rm HPO}_{4}^{2-}} \right) \frac{10^{({\rm pK}_{\rm A1^{*}} - {\rm pH})}}{1 + 10^{({\rm pK}_{\rm A1^{*}} - {\rm pH})}} + \\ & \Phi_{\rm F}({\rm HQ}^{+})_{{\rm HPO}_{4}^{2-}} - \frac{10^{({\rm pK}_{\rm A2^{*}} - {\rm pH})}}{1 + 10^{({\rm pK}_{\rm A2^{*}} - {\rm pH})}} \end{split}$$
(S3.1)

Here  $H_2Q^{2+}$ ,  $HQ^+$  and Q are the protonated quinolinium probe, the quinolinium probe and the deprotonated probe, respectively, as depicted in Figure 3.1.  $\Phi_F(H_2Q^{2+})_{H_2PO_4}^-$  is the fluorescence quantum yield of  $H_2Q^{2+}$  in the presence of dihydrogen phosphate anions  $(H_2PO_4^{2-})$ , species that do not quench the fluorescence.  $\Phi_F(H_2Q^{2+})_{HPO_4^{2-}}$  and  $\Phi_F(HQ^+)_{HPO_4^{2-}}$  are the fluorescence quantum yields of  $H_2Q^{2+}$  and  $HQ^+$ , in the presence of hydrogen phosphate ions  $(HPO_4^{-2})$ and these values depend on the buffer concentration.  $pK_{A1^*}$  and  $pK_{A2^*}$  are the excited state dissociation constants of the  $H_2Q^{2+}/HQ^+$  and  $HQ^+/Q$  equilibria, respectively and  $pK_{A2}$  is the second dissociation constant of phosphoric acid with a values between 6.2-7.2.



Figure S3.1: Normalised fluorescence intensity and lifetime of probe **2b** in 0.1 M and 0.1 mM phosphate buffer. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.5 for more information.

Parameters obtained from Figure S3.1: Intensity versus pH with 0.1 mM Phosphate buffer, using Eq S3.1:

- $pK_A = 6.5$ ,  $pK_{A1^*} = 9.4$ ,  $pK_{A2^*} = 12.2$
- $\Phi_F(H_2Q^{2+})_{H_2PO_4^-} \Phi_F(H_2Q^{2+})_{HPO_4^{2-}} = 0.025$
- $\Phi_F(H_2Q^{2+})_{HPO_4^{2-}} \Phi_F(HQ^+)_{HPO_4^{2-}} = 0.75$
- $\Phi_{\rm F}({\rm HQ^+})_{{\rm HPO_4^{2-}}} = 0.225$

Lifetime versus pH with 0.1 M Phosphate buffer, using Eq S3.5:

•  $pK_A = 6.4$ ,  $pK_{A1^*} = 10.6$ ,  $pK_{A2^*} = 12.5$ 

Lifetime versus pH with 0.1 mM Phosphate buffer, using Eq S3.4:

•  $pK_{A1*} = 9.7$ ,  $pK_{A2*} = 12.4$ 



Figure S3.2: Normalised fluorescence intensity and lifetime of probe **2d** in 0.1 M and 0.1 mM phosphate buffer. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.5 for more information.

Parameters obtained from Figure S3.2: Intensity versus pH with 0.1 mM Phosphate buffer, using Eq S3.1:

- $pK_A = 7.15, pK_{A2^*} = 11.3$
- $\Phi_F(H_2Q^{2+})_{H_2PO_4^-} \Phi_F(H_2Q^{2+})_{HPO_4^{2-}} = 0.12$
- $\Phi_{\rm F}({\rm HQ^+})_{{\rm HPO_4}^{2-}} = 0.88$

Lifetime versus pH with 0.1 M Phosphate buffer, using Eq S3.5:

•  $pK_A = 6.0, pK_{A2^*} = 11.9$ 

Lifetime versus pH with 0.1 mM Phosphate buffer, using Eq S3.4:

•  $pK_{A2^*} = 11.5$ 



Figure S3.3: Normalised fluorescence intensity and lifetime of probe **2e** in 0.1 M and 0.1 mM phosphate buffer. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.5 for more information.

Parameters obtained from Figure S3.3: Intensity versus pH with 0.1 mM Phosphate buffer, using Eq S3.1:

- $pK_A = 6.15, pK_{A2^*} = 11.7$
- $\Phi_{\rm F}({\rm H_2Q^{2+}})_{{\rm H_2PO_4}^-} \Phi_{\rm F}({\rm H_2Q^{2+}})_{{\rm HPO_4^{2-}}} = 0.025$
- $\Phi_{\rm F}({\rm HQ^+})_{{\rm HPO_4}^{2-}} = 0.975$

Lifetime versus pH with 0.1 M Phosphate buffer, using Eq S3.5:

•  $pK_A = 7.1$ ,  $pK_{A2^*} = 11.8$ 

Lifetime versus pH with 0.1 mM Phosphate buffer, using Eq S3.4:

• pK<sub>A2\*</sub> = 11.9



Figure S3.4: Normalized fluorescence lifetime vs pH for probes **2a-2e** in a 0.1 mM Phosphate buffer. Curves connecting the data points were obtained by using Equation S3.4 or S3.5. Error bars are not included for better readability.



Figure S3.5: Normalised fluorescence intensity and lifetime of probe **2d** in water containing 0.1 mM phospate buffer. The curves connecting the data points are generated using Eq. 3.5 and the equations in 3.5.3. The error bars in this graph are the standard deviation from the FLIM measurement. See 3.5.5 for more information.



Figure S3.6: Fluorescence lifetime  $\tau$ F vs temperature of probe **2b** in demineralised water. The lifetime vs temperature slope is -0.045 ns/°C.



Figure S3.7: Fluorescence lifetime  $\tau$ F vs temperature of probe **2d** in demineralised water. The lifetime vs temperature slope is -0.060 ns/°C.



Figure S3.8: Phosphate dependent fluorescence lifetime of probe 2b and 2d in water at pH = 7.5-8.



Figure S3.9: Sulphate dependent fluorescence lifetime of probe **2d** at pH = 7 and pH = 3.5, the solution was acidified with sulfuric acid to get the pH 3.5 solution.  $10^{-4}$  M phosphate buffer was added to stabilize the pH.

#### **3.5.2.** PHOTOPHYSICS OF HQ AND Q AT HIGH PH VALUES

The photophysics of alkylated quinolinium probes is depicted in Figure S3.10. Here  $k_{\rm F}$  and  $k_{\rm IC}$  are rate constants for fluorescence and non-radiative decay by internal conversion, respectively.  $r_{\rm ESPT}$  and  $r_{\rm GSPT}$  are the rates of excited state proton transfer and ground state proton transfer.  $K_{\rm A2}$  and are  $K_{\rm A2^*}$  are the acid dissociation constants in the ground and the excited state, respectively.

In the ground state  $HQ^+$  is the only species that is detected by absorption spectroscopy. This is the case because  $pK_A$  has a value well above 14. In the excited state, the equilibrium composition is determined by equation S2 in which  $pK_{A2^*}$  has values between 11.5 and 12.5.

$$\frac{[HQ^{+*}]}{[HQ^{+*}] + [Q^{*}]} = \frac{10^{(pK_{A2^{*}} - pH)}}{1 + 10^{(pK_{A2^{*}} - pH)}}$$
(S3.2)

At pH values well below  $pK_{A2^*}$  only  $HQ^{**}$  is formed, because there is no driving force for deprotonation in the excited state according to Eq. S2. At pH values well above  $pK_{A2^*}$ , non-emissive



Figure S3.10: Photo physics of 1-methyl-7-aminoquinolinium probes at high pH values.

 $\mathbf{Q}^*$  is formed exclusively upon excitation of  $\mathbf{HQ}^+$ . This is the case because the  $[\mathbf{HQ}^{+*}]/[\mathbf{Q}^*]$  ratio described by Eq. S2 approaches 0 and because at high pH values the rate of deprotonation  $r_{\text{ESPT}}$  (=  $k_{\text{ESPT}}$  [OH<sup>-</sup>]) is high enough to fully deprotonate  $\mathbf{HQ}^{+*}$  during its lifetime. At pH values close to pK<sub>A2\*</sub>, mixtures compose of  $\mathbf{HQ}^{+*}$  and  $\mathbf{Q}^*$  will be formed. The ratio  $[\mathbf{HQ}^{+*}]/[\mathbf{Q}^*]$  will be determined by the equilibrium ratio described by Eq. S2, the rate of deprotonation  $r_{\text{ESPT}}$  and the excited state lifetime that is available to reach equilibrium. If the ESPT process is fast compared to the lifetime, i.e.  $r_{\text{ESPT}} \approx k_{\text{IC}}$ , the equilibrium constant  $K_{\text{A}^*}$  measured from intensity versus pH plots will equal  $K_{\text{A2*}}$ . If the ESPT process proceeds slower, deprotonation lags behind and the apparent dissociation pK<sub>A\*</sub> will have a higher value.

When  $pK_A = pK_{A^*}$  (no ESPT), "static" mixtures of  $HQ^{+*}$  and  $Q^*$  are formed intensities go down as the  $[HQ^{+*}]/[Q^*]$  ratio decreases. Lifetimes, however, stay constant because only  $HQ^{+*}$  has a finite lifetime. For that reason ESPT is a prerequisite for lifetime dependence if one of the species, Q in this case, is non-fluorescent. The expression for the lifetime of  $HQ^{+*}$  is given in Equation S4:

$$\tau_{\rm F} = \frac{k_{\rm F}}{k_{\rm F} + k_{\rm IC} + r_{\rm ESPT}} \tag{S3.3}$$

In this Equation  $k_{\rm F}$  and  $k_{\rm IC}$ , are rate constants for fluorescence and non-radiative decay by internal conversion.  $r_{\rm ESPT}$  is the rate of excited state proton transfer. In equation S4,  $r_{\rm ESPT}$  is the unknown.  $r_{\rm ESPT}$  is proportional to  $[OH^-]$  and we can write the equation  $r_{\rm ESPT} = k_{\rm ESPT}[OH^-]$ . However, in this equation  $k_{\rm ESPT}$  is a rate "constant" that is pH dependent, is the unknown. As is the case in the intensity measurements, a slower ESPT process will result in a higher experimental pK<sub>A\*</sub> value. In a follow-up manuscript we will address the kinetics of the ESPT process.



#### **3.5.3.** Absorption and Fluorescence spectra

Figure S3.11: UV-Vis Absorption spectra of quinolinium probes **2a-2e** in 0.1mM Phosphate buffer. pH 2.5 was achieved by addition of 0.025 M HCl, pH 13 was achieved by addition of 0.1 M KOH until pH was reached



Figure S3.12: Fluorescence emission spectra of quinolinium probes 2a-2e in 0.1mM Phosphate buffer

#### **3.5.4.** FITTING THE FLUORESCENCE LIFETIME VS PH CURVES

Fluorescence lifetime curves were fitted using Equation S3.4 that is similar to Equation 3.5, that we used for fitting fluorescence intensity curves. Equation S3.4 lacks a solid physical foundation, because lifetimes are proportional to the concentrations of the constituents in a mixture. Still Eq. S3.4 provides excellent fitting curves and the obtained pKA\* values and lifetime enhancements are reported in Table 3.1.

$$\tau_{\rm F} = \left(\tau_{\rm F}({\rm H_2Q^{2+}}) - \tau_{\rm F}({\rm HQ^+})\right) \frac{10^{p{\rm K_{A1^*}} - p{\rm H}}}{1 + 10^{p{\rm K_{A1^*}} - p{\rm H}}} + \tau_{\rm F}({\rm HQ^+}) \frac{10^{p{\rm K_{A2^*}} - p{\rm H}}}{1 + 10^{p{\rm K_{A2^*}} - p{\rm H}}} \tag{S3.4}$$

In case phosphate quenching occurs Equation S3.4 will be expanded, analogous to the expansion of Equation 3.5 to Equation S3.1, and Equation S3.5 is obtained:

$$\begin{aligned} \tau_{\rm F} &= \left(\tau_{\rm F}({\rm H_2Q^{2+}})_{{\rm H_2PO_4^{-}}} - \tau_{\rm F}({\rm H_2Q^{2+}})_{{\rm HPO_4^{2-}}}\right) \frac{10^{({\rm pK_{A2}}-{\rm pH})}}{1+10^{({\rm pK_{A2}}-{\rm pH})}} + \\ & \left(\tau_{\rm F}({\rm H_2Q^{2+}})_{{\rm HPO_4^{2-}}} - \tau_{\rm F}({\rm HQ^+})_{{\rm HPO_4^{2-}}}\right) \frac{10^{({\rm pK_{A1^*}}-{\rm pH})}}{1+10^{({\rm pK_{A1^*}}-{\rm pH})}} + \\ & \tau_{\rm F}({\rm HQ^+})_{{\rm HPO_4^{2-}}} - \frac{10^{({\rm pK_{A2^*}}-{\rm pH})}}{1+10^{({\rm pK_{A2^*}}-{\rm pH})}} \end{aligned}$$
(S3.5)

The symbols used in Eq. S3.5 are explained in sections 3.5.3 and 3.5.1.

#### **3.5.5.** Synthesis of probe 2e

Synthesis steps of **2e** (7-(Hexylamino)-1-methylquinolinium Iodide): 7-Fluoro-1-methylquinolinium iodide (1, 250 mg, 0.86 mmol), hexylamine (120 mg, 1.2 mmol), and triethylamine (95 mg, 94 mmol) in 100% ethanol (3 mL) were heated to reflux for 30 min. The reaction mixture was allowed to cool to room temperature. After addition of 1 mL of diethyl ether, orange crystals were formed and 260 mg (82%) of **2e** was obtained after filtration. For the NMR data, please refer to the SI of [48].

#### **3.5.6.** TOGGEL FLIM CAMERA SETTINGS AND SETUP

All lifetime measurements were performed with a Toggel FLIM camera. The solutions were placed in a cuvette and an image was taken at the following experimental settings:

- · 20 MHz laser modulation frequency
- 12 Phases (12 images taken to fit the lifetime)
- 50 ms Exposure time
- Image intensifier gain 2
- · 300 mW Laser power
- 5x zoom lens on the microscope

The LIFA software calculates the lifetime from the phase shift of the laser at every pixel. The lifetimes shown in the figures (i.e. Figure 3.4) were calculated by taking an average over all the pixels (Figure S3.13). This method is also known as the "Frequency domain". *Note on the error bars:* 

The error bars in all graphs are the standard deviations of the FLIM measurements. We acknowledge that the error bars of our measurements (in figures 4, 5, 6, S1-S7) are relatively high. The two main reasons for this are:



Figure S3.13: Example of a lifetime measurement in the LIFA software. The measured lifetime is an average of the majority of the pixels in the screen.

- At high lifetimes (>10 ns) The FLIM camera calculates the lifetime at >200000 pixels and takes an average over all these pixels to calculate the average lifetime (Figure S18). However, exponential decay is a random process and at every pixel the lifetime can therefore be slightly different. At larger lifetimes the excited state molecule is more stable and therefore results in a larger spread of times (which in turn results in a larger standard deviation). Also, in all measurements the modulation frequency was 20 MHz, which is optimal for detecting lifetimes of around 8 ns. The higher lifetimes (12 ns+) would be more accurate if a modulation frequency of 15 MHz was used.
- At low light intensities At low light intensities we also observed large standard deviation, this is mainly due to the poor signal to noise ratio at these conditions. The noise in the measurements was usually around 50-100 counts, which was similar to the signal at the lower fluorescence intensities.

The setup is shown in Figure S3.14.

A more standard method of determining the lifetime of a fluorescent probe is by looking at the exponential decay of the light intensity, which is also known as the "Time domain". In order to translate lifetimes to pH values reliably, we have compared lifetimes measured in the time domain with those measured in the frequency domain on our FLIM microscope setup. The data collected for probe **2b**, presented in Figure S3.15, demonstrate that lifetimes determined by both methods are almost identical.



Figure S3.14: Photograph of the FLIM lifetime measuring setup. A. Zeiss Axiovert 200m Microscope to which everything is attached B. Objective and 3D printed sample holder C. CrestOptics X-Light V2 spinning disk confocal unit, the 405 nm laser is connected at the back D. Lambert Instruments Toggel FLIM camera.



Figure S3.15: Comparison of fluorescence lifetime of probe **2b** in a 0.1 M phosphate buffer as a function of pH measured using time domain (black squares) or frequency domain (red circles) measurements.

### **3.6.** SUPPLEMENTARY VIDEOS



 $\label{eq:Video} Video~S3.16: pH vs time video of a CO_2 \ bubble \ dissolving in the surrounding \ KOH \ liquid. \ https://www.youtube.com/watch/Zs37uDybhQI$ 



Video S3.17: pH vs time video of BaOH diffusion from a paper bag into the surrounding liquid. https://www.youtube.com/watch/JhYEKTM1Ljc

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# 4

# BUBBLE-INDUCED MASS TRANSPORT AT VERTICAL HYDROGEN EVOLVING ELECTRODES



This chapter is being prepared for submission to Nature Chemical Engineering as:

Bubble-induced mass transport at vertical hydrogen evolving electrodes.

Jorrit Bleeker, Florianne M. Wiegel, Aron P. Kahn, J.W. (Willem) Haverkort, Christiaan V. Schinkel, Maxime Hoogland, Lorenz M. Baumgartner, Wolter F. Jager, J.R. (Ruud) van Ommen, David A. Vermaas Gas-evolving electrodes, for example in electrolysis applications, benefit from enhanced mass transport driven by the movement of gas bubbles. To maximize this "bubble-induced mass transport", we need to better understand the underlying processes. Here, we present an optical investigation of microscale mass transport processes at vertical hydrogen evolving electrodes. Using fluorescence lifetime imaging microscopy (FLIM), we show that the boundary layer thickness at a Pt wire electrode is mainly reduced by bubble detachment. Next, velocity profiles were measured around bubbles at a nickel plate electrode using micro-particle image velocimetry ( $\mu$ PIV) and integrated into a mass transport model. This showed that both bubble detachment and wake flow have large impact on improving mass transport. Our observations also showed that "single bubble"-events do not exist at vertical electrodes, due to the frequent wake flow events from passing bubbles, even at low current densities (< 5 mA cm<sup>-2</sup>).

#### 4.1. INTRODUCTION

Gas-evolving electrochemical processes, such as water electrolysis<sup>[1]</sup>, electrochemical  $CO_2$  reduction ( $CO_2R$ )<sup>[2]</sup>, and electrochemical  $CO_2$  capture<sup>[3]</sup> are essential for a successful energy transition. Electrochemically produced gas bubbles typically have a bad reputation, as the bubbles can block the active sites of the electrode and increase the cell resistance by reducing the electrolyte conductivity<sup>[4–7]</sup>. This results in a higher cell voltage and hence in higher electrolyzers. Firstly, detached gas bubbles can remove other bubbles by dragging them along or by coalescence. Secondly, gas bubbles will create convection by growing, coalescing and moving through the electrolyte, thereby alleviating mass transport limitations<sup>[6, 8, 9]</sup>.

This "bubble-induced transport" improves the transport of dissolved species to and from gas-evolving electrodes. This is particularly useful in aqueous  $CO_2R$ , where the improved transport of  $CO_2$  to the electrode allows the system to operate at higher current densities[10, 11]. Also alkaline water electrolyzers benefit from enhanced mass transport, because dissolved H<sub>2</sub> and O<sub>2</sub> are transported away from the electrode, this reduces electrode overpotential, crossover of gasses and improves safety[12–14]. Finally, bubble-induced transport can also reduce in the pH build-up at the electrode surface, which reduces the Nernstian overpotentials for systems operating at near-neutral pH[11].

Having established that bubble-induced mass transport is important, we need to know how to better leverage its effects. The transport has described in equations in the works of Janssen[15–17], Tobias[18], Vogt[19] in the 1980s, and more recently by Vogt[9] and Haverkort [8, 20], which are usually fitted to mass transport data from boundary layer experiments with indicator ions (e.g.,  $Fe^{2+/3+}$  or  $Fe(CN)_6^{3+/4+}$ )[16, 21]. Although this method is statistically robust, it provides limited insights into the underlying microscale processes that drive the mass transport, such as bubble growth, detachment, wake flow and Marangoni vortices[15, 19, 22, 23] (see Figure 4.1).



Figure 4.1: Proposed micro-convective mixing mechanisms at gas-evolving electrodes A. Refreshment of electrolyte after bubble detachment[22] B. Convection generated by growing bubbles[19] C. Wake flow around rising gas bubbles[15] D. Marangoni convection at the base of a gas bubble[23]. Figure inspired by Zhao et al.[6]

Good understanding of the micro-scale processes is crucial when one wants to extrapolate the equations to different current densities, flow conditions or alternative electrode geometries. While significant effort has been made to better understand these micro-processes through computational modelling[24–26], realistic modelling of moving gas bubbles at vertical electrodes remains challenging. Also experimental investigation on these microprocesses is limited, and has primarily been obtained through optical methods like particle tracking[23, 27, 28] and fluorescence[29], and are mostly limited to horizontal (micro) electrodes and low current densities[23, 30–33].

In this work, our objective is to analyse the micro-processes of bubble-induced mass transport at vertical hydrogen evolving electrodes at current densities up to 40 mA cm<sup>-2</sup>. To this end, we present an optical analysis of bubble-induced mass transport using Fluorescence Lifetime Imaging Microscopy (FLIM) and micro-Particle Image Velocimetry ( $\mu$ PIV). We first use FLIM to visualize the development of the boundary layer at a Pt wire electrode and demonstrate that gas bubble detachment is dominant for confining the boundary layer thickness. We then apply  $\mu$ PIV to determine the velocity fields near a hydrogen-evolving Ni plate electrode. These velocity fields are integrated into a simple mass transport model to calculate the diffusion boundary layer thickness under conditions of bubble growth, detachment, and wake flow. Finally, we discuss the influence of bubble diameter on mass transport and outline the limitations of these techniques when applied at higher current densities.

#### **4.2.** METHODS

#### 4.2.1. FLIM EXPERIMENTS

Water electrolysis with operando fluorescence lifetime imaging microscopy was performed in the electrochemical cuvette cell shown in Figure 4.2A. This setup consists of two Pt wires, 300  $\mu$ m diameter and 2.6 cm deep in electrolyte (~0.25 cm<sup>2</sup> electrode area) in a polystyrene cuvette (1x1x3 cm<sup>3</sup>), filled with 0.2 M K<sub>2</sub>SO<sub>4</sub> and 100  $\mu$ M FLIM probe 2b from Bleeker et al.[34] (Figure 4.2B). The FLIM camera was connected on a microscope with a 2.5x objective, in which the cuvette could be mounted. The objective has a scale factor of 0.105 pixel  $\mu$ m<sup>-1</sup>. The total image size was 504 x 512 pixels or 4.79 x 4.86 mm<sup>2</sup>. The lifetime was recorded with every 2.9 s and converted into pH with the calibration curve in Figure 4.2B. See 4.5.1 and previous publications from our group[34] for more information on the setup.

During the boundary layer analysis, we focused the microscope objective to the cathode while applying a negative current (-4, -8 and -16 mA cm<sup>-2</sup> for 2 minutes with 30second pauses at 0 mA cm<sup>-2</sup>). The current was controlled with a potentiostat (Ivium CompactStat.h10800).

#### **4.2.2.** $\mu$ **PIV** EXPERIMENTS

The  $\mu$ PIV experiments were performed in an electrochemical flow cell, which allowed us to apply a forced convection (Figure 4.2C). This cell consisted of two transparent acrylate (PMMA) flow channels (0.4x0.4 cm<sup>2</sup> wide, 8 cm long), supported by two 3D printed PMMA backplates. The flow channels were milled with a special diamond mill to create optical transparency. Silicone gaskets (0.5 mm thickness) were used for sealing.

The flow channels, while composed of two separate parts, were not physically separated, thus forming a single continuous channel. Two nickel plate (99.5%, Thermo Scientific) electrodes were used as anode and cathode, which were milled in such a way that  $0.4 \text{ x} 3 \text{ cm}^2$  of the electrode was protruding into the flow channels, while the remaining area of the electrode was covered with gaskets, resulting in an active area of  $1.2 \text{ cm}^2$  (Figure 4.2D).



Figure 4.2: A. Electrochemical cuvette cell used in FLIM experiments B. Fluorescence lifetime ( $\tau_{\phi}$ ) vs pH calibration curve of FLIM probe 2b from Bleeker et al.[34] C. Electrochemical flow cell used in the  $\mu$ PIV experiments D. Side cross-section view of the assembled electrochemical flow cell. See 4.5.1 for a photograph of the assembled cell.

During the  $\mu$ PIV experiments we pumped electrolyte (1 M KOH with Rhodamine 6G fluorescent particles, with 2  $\mu$ m diameter) with a NE-1000 syringe pump (1 to 9 mL min<sup>-1</sup>). We used a long 1/16" tube at the inlet to create a large pressure drop and minimize fluctuations in the flowrate[35]. The electrodes were connected to the potentiostat (Ivium CompactStat.h10800) with copper wires through the backplate of the cell. The electrodes were connected with two wires each to operate the electrochemical cell under a 4-electrode configuration. Gas evolution was controlled by applying a constant current (0.5 to 50 mA cm<sup>-2</sup>) for 100 seconds.

The µPIV data was collected with a Lavision Imager Intense CCD camera (5 double

frames s<sup>-1</sup>) in combination with a New Wave Nd YAG laser. The laser shoots two pulses separated by 0.5-10 ms time interval, during the pulses the camera records two images. The time between two pulses was adjusted to ensure particles moved less than <sup>1</sup>/<sub>4</sub> interrogation window to follow PIV best practises[36]. The camera and laser were connected to the Zeiss Axiovert 200 M microscope with a 10x/0.30 objective, a dichromatic mirror (LP590) and a beam splitter (FT580) (see 4.5.1). The 10x/0.30 objective has a scale factor of 1.59 pixel  $\mu$ m<sup>-1</sup>. The total image size was 1376 x 1040 pixels or 863  $\mu$ m x 652  $\mu$ m. The data was processed with DaVis software from LaVision, see 4.5.2 for an explanation of the method, pre-treatment steps, calibration and the PIV settings.

#### 4.2.3. MASS TRANSPORT MODEL

The velocity fields measured with  $\mu$ PIV were translated into bubble-induced mass transport with a 2D model in COMSOL Multiphysics, through a continuum modelling approach. The model simulates OH<sup>-</sup> diffusion from an electrode into the bulk electrolyte (i.e., simulating a proton-coupled electron transfer cathode[10]). The velocity profile from the  $\mu$ PIV measurements was imported into COMSOL and interpolated across the entire domain. A 2D concentration field was calculated under these conditions. The model is governed by Eq 4.1:

$$0 = \nabla \cdot (D_{\text{OH}} \nabla c - \mathbf{v}c) \tag{4.1}$$

and the following boundary conditions:

$$c(x=0, y) = c^0 \tag{4.2}$$

$$c\left(x=L,y\right)=0\tag{4.3}$$

$$c(x, y = 0) = c(x, y = H)$$
 (4.4)

Here  $D_{OH}$  is the diffusion coefficient of OH<sup>-</sup>, *c* is the concentration, **v** is the 2D velocity field obtained from µPIV,  $c^0$  is the OH<sup>-</sup> concentration at the electrode surface and L and H are the width and height of the visualized area. Eq 4.4 is a periodic boundary condition where the source is at y = 0 and the sink at y = H. We acknowledge that these equations strongly simplify a water electrolysis system, and serve only to understand the magnitude of mass transport from the obtained velocity fields from µPIV. See 4.5.3 for detailed information on the modelling steps.

#### 4.3. RESULTS

#### 4.3.1. BOUNDARY LAYER FORMATION AT A PT WIRE ELECTRODE

To investigate bubble-induced mass transport at an electrode, we visualize the development of an OH<sup>-</sup> boundary layer, formed at a Pt wire acting as a cathode in 0.2 M K<sub>2</sub>SO<sub>4</sub> electrolyte (Figure 4.3A). The boundary layer was visualized using Fluorescence Lifetime Imaging Microscopy (FLIM). We use 100  $\mu$ M of a tailor-developed FLIM dye, labelled as dye 2b from Bleeker et al.[34], which allows us to resolve the pH from 8 to 13.5 (Figure 4.2B) and subsequently convert these values to OH<sup>-</sup> concentration by using  $c_{OH} = 10^{pH-14}$ .

Figure 4.3B shows the development of the OH<sup>-</sup> boundary layer thickness ( $\delta$ ) when a cathodic current is applied. The typical development of the boundary layer (at 4, 8 and 16 mA cm<sup>-2</sup>) is demonstrated in a video of the 2D pH profiles, which can be found in section 4.6. This time- and space-resolved pH mapping, with a pixel resolution of 10  $\mu$ m, emphasizes the power of FLIM as a tool to analyse mass transport.

The boundary layer thickness ( $\delta$ ) is defined as the region where the normalized OH<sup>-</sup> concentration decreases by 95% of the surface OH<sup>-</sup> concentration. The OH<sup>-</sup> concentration at the surface fluctuated around 4 mmol OH<sup>-</sup> L<sup>-1</sup> (see 4.5.4 for  $c_{OH}$  plots), which makes the threshold for  $\delta$  approximately 0.2 mmol OH<sup>-</sup> L<sup>-1</sup>. Inside the boundary layer OH<sup>-</sup> transport is mainly governed by diffusion, the contribution from migration is negligible since the main charge carriers are K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions at neutral pH (the transport number of OH<sup>-</sup> is <1%). Since diffusive mass transport scales with 1/ $\delta$ , we calculate the effective boundary layer thickness ( $\delta_{eff}$ ) as the harmonic average over the electrode height (*y*):

$$\delta_{\rm eff} = \frac{L}{\int_0^L \frac{1}{\delta(y)} \mathrm{d}y} \tag{4.5}$$

Where *L* is the length of the visualized electrode and  $\delta(y)$  is the boundary layer thickness at height *y*.

Initially, at 4 mA cm<sup>-2</sup>,  $\delta_{\text{eff}}$  grows with  $\sqrt{D_{\text{OH}}t}$  according to the penetration theory (Figure 4.3B), until the first bubbles start to form around 75 s (Figure 4.3C). After 75 s, the boundary grows at a smaller rate, which could indicate micromixing caused by the growth of stationary gas bubbles. The surface pH increases up to around 12, and  $\delta_{\text{eff}}$  becomes around 1 mm. The lower pH observed in the gas bubbles is an optical artifact; the bubbles act as lenses and reflect light from the bulk electrolyte.

The  $\delta_{\text{eff}}$  is smaller at higher current densities (Figure 4.3D), which agrees with the findings of previous studies[8]. This is due to gas bubbles breaking up the boundary layer, which enhances transport during their detachment (Figure 4.3E). This is further highlighted in Figure 4.3B, where the boundary layer thickness reduces most after bubble detachments. In more detail, the 2D FLIM images show that higher current densities create pH profiles with a thinner, more fluctuating boundary layer with higher pH near the surface (Figure 4.3C-E).



Figure 4.3: Boundary layer visualization experiments at a H<sub>2</sub> evolving Pt wire electrode in 0.2 M K<sub>2</sub>SO<sub>4</sub>. The pH was obtained using FLIM and 100  $\mu$ M of quinolinium pH probe (see Figure 4.2B) A. Image of the Pt wire and H<sub>2</sub> bubbles during the experiment B. OH<sup>-</sup> boundary layer thickness ( $\delta_{eff}$ ) development over time at different applied constant current densities. FLIM obtained pH profiles during C. an applied current, showing growth without effects from gas bubbles, D. for increasing current densities, E. before, during and after bubble detachment. See 4.5.4 for  $c_{OH}$  plots for various timestamps during the measurement.

#### 4.3.2. Fluid flow around gas bubbles at a Ni plate electrode

Our FLIM experiments show that gas bubbles are effective at reducing the boundary layer thickness. To further gain insights into the microprocesses that occur during gas evolution, we analysed the fluid flow during electrolysis using micro Particle Image Velocimetry ( $\mu$ PIV). We focused on a 0.6 x 0.8 mm<sup>2</sup> area adjacent to a flat nickel electrode immersed in 1 M KOH operating at 2.5 mA cm<sup>-2</sup> with an electrolyte flowrate of 5 mL min<sup>-1</sup> (Figure 4.4A).

We implement the velocity fields obtained from  $\mu$ PIV in a simple steady state 2D mass transport model in COMSOL to calculate the corresponding mass transport rates. We applied a forced convection (3 to 5 mL min<sup>-1</sup>, average velocity: 1.6 to 2.6 mm s<sup>-1</sup>, *Re* = 8 to 14) which also serves to minimize the effects of natural convection due to heating from the light source (see 4.5.5 for validation of the  $\mu$ PIV and the modelling method). Our mass transport model ignores the presence of the gas bubble and assumes electrolyte in the entire domain. This assumption will no longer hold for large bubbles or large gas fractions in the observed area.

Figure 4.4A and B show three consecutive frames and x-velocity fields before, during and after the detachment of a H<sub>2</sub> bubble. During the bubble growth, fluid is flowing around the bubble, hindering the mass transport below the bubble. This is reflected in the relatively thick boundary layer (Figure 4.4C, first panel). During bubble detachment, a strong flow occurs around the bubble with lateral velocities of an order of magnitude larger than during bubble growth, resulting in the smallest boundary layer (Figure 4.4C, second panel). Subsequent wake flow results in a flow towards the electrode, which keeps the boundary layer small after bubble departure (Figure 4.4C, third panel). The effects of wake flow can be observed for 1 to 2 frames (0.2 - 0.4 s) after bubble detachment. The detachment and subsequent wake flow disrupt the boundary layer above the bubble ble and a distance of approximately one bubble diameter ( $d_{Bubble}$ ) below the gas bubble. Beyond this region, the boundary layer thickness remains relatively unaffected, which can also be observed in the FLIM experiments in Video S4.10.

The bubble-induced mass transport from bubble nucleation (t = 0 s) up to bubble detachment and wake flow is shown in Figure 4.4D. We use  $1/\delta_{\text{eff}}$  as a metric to quantify the mass transport, since diffusive mass flux scales with  $1/\delta$ . The base case, when a velocities of zero (**v** = 0) are given as an input of the simulation, resulted in a  $1/\delta_{\text{eff}}$  of 1.32 mm<sup>-1</sup>. Using the measured velocity field associated to forced convection of 5 mL min<sup>-1</sup>, without gas evolution (0 mA cm<sup>-2</sup>), causes  $1/\delta_{eff}$  to slightly increase to 1.38 ± 0.06 mm<sup>-1</sup>, and hence has a small effect on the resulting mixing. This increase is a result of small velocity fluctuations and errors in the measured x-velocity ( $v_x$ ). At 2.5 mA cm<sup>-2</sup>, the values for  $1/\delta_{\rm eff}$  are significantly higher, 3.66 ± 1.24 mm<sup>-1</sup>, compared to the case without applied current density (Figure 4.4D). During bubble detachment and subsequent wake flow, the mass transport is 4-6 times larger compared to a system without gas evolution. This aligns with the observations in the FLIM analysis, where the boundary layer is consistently thinnest after bubble detachment and wake flow (Figure 4.3B). Similar results are obtained for repeated experiments and at different flow rates (Figure 4.4E): the largest peaks in  $1/\delta_{\text{eff}}$  correspond to cases of bubble detachment, and are rather independent of the forced convection flow rate, as previously also explained by Janssen [37, 38].



Figure 4.4:  $\mu$ PIV investigation of a H<sub>2</sub> evolving Ni plate electrode (1 M KOH, 2.5 mA cm<sup>-2</sup>, 5 mL min<sup>-1</sup> flowrate) A. Images during bubble growth, detachment and wake flow of a H<sub>2</sub> bubble, the small white dots are PIV particles B. Velocity fields at the electrode obtained with  $\mu$ PIV. Streamlines indicate the flow direction, the color contour is the velocity component in the x-direction C. Dimensionless OH<sup>-</sup> concentration fields, obtained after implementing the velocity fields into the mass transport model model, the dashed line indicates the boundary layer thickness D. Mass transport, expressed as  $1/\delta_{eff}$ , during bubble evolution with an electrolyte flowrate of 5 mL min<sup>-1</sup> (the datapoints with timestamps correspond to those in Figure A, B and C) E.  $1/\delta_{eff}$  for two additional datasets at 2.5 mA cm<sup>-2</sup> at different flowrates.

Additionally, Figure 4.4D and E highlight that an isolated "single bubble" does not really exist on vertical electrodes at relevant current densities, which can be deduced from the large amount of peaks in  $1/\delta_{eff}$ . The peaks, for example at 1.4 s and 2.2 s in Figure 4.4D, are a result of the wake flow of passing bubbles (see Video S4.11 & S4.12). Although the largest peaks are caused by bubble release in the direct vicinity, the effect of passing bubbles leads to a 2-3 times better mass transport compared to the case without applied

current density [37, 38]. Moreover, passing bubbles also increase the chance of another bubble-release event when hit by a passing bubble. Hence, even at a small 1.2 cm<sup>2</sup> electrode and low current densities ( $<5 \text{ mA cm}^{-2}$ ) the effect of wake flow of other bubbles significantly affects the mass transport. We conclude that industrially relevant research on mass transport at gas-evolving electrodes should always be done including a large number of bubbles at a substantial electrode size. These findings agree with the model of Haverkort[8], which states that a H<sub>2</sub> evolving electrode in KOH mainly experiences mixing due to natural convection from rising gas bubbles.

We did not observe large effects of bubble growth on the mass transport. Also, we did not detect large velocity fields on the 1-5 mm s<sup>-1</sup> scale that correspond to Marangoni convection, as reported by Yang and Eckert[23]. Hence, we believe that the effect of Marangoni convection is minor regarding mass transport on plate electrodes. The large difference in velocities could be explained to differences in experimental setups, as their use of a microelectrode likely produces stronger local concentration and temperature gradients.

#### 4.3.3. EFFECT OF BUBBLE DIAMETER ON MASS TRANSPORT

The microprocesses during bubble-induced mass transport are known to strongly depend on  $d_{\text{bubble}}[10, 16, 39]$ . Therefore, we relate our measured diffusion boundary layer thickness (inferred from FLIM) and flow velocities (inferred from  $\mu$ PIV) to  $d_{\text{bubble}}$ .

Figure 4.5A shows the reduction of the boundary layer thickness upon detachment of a H<sub>2</sub> bubble with diameter  $d_{\text{bubble}}$  during the FLIM experiment. Although some scattering occurs, the strongest reduction in boundary layer thickness correlates to the detachment events of the largest bubbles ( $d_{\text{bubble}}$  450-500 µm). These findings align with the model proposed by Ibl et al.[22], which proposes that during gas bubble detachment, the bubble is completely replaced by fresh electrolyte. Therefore, larger bubbles enhance mass transport more effectively by refreshing a larger volume of electrolyte at the electrode surface.

Additionally, larger gas bubbles also travel faster. The terminal velocity ( $v_t$ ) of a rising bubble in free electrolyte scales with  $d_{\text{bubble}}^2$ , ref[40]:

$$v_t = \frac{g}{18\mu} d_{\text{bubble}}^2 \left(\rho_{\text{L}} - \rho_{\text{G}}\right) \tag{4.6}$$

Here *g* is the gravitational constant (9.81 m s<sup>-2</sup>),  $\mu$  the dynamic viscosity in Pa·s, and  $\rho_{\rm L}$  and  $\rho_{\rm G}$  are the densities of the electrolyte and gas, respectively. (Note that this equation is valid for Stokes flow, for bubbles with a Reynolds number of < 1 or  $d_{\rm bubble}$  < 120  $\mu$ m.) In  $\mu$ PIV measurements we observed that the maximum y-velocity of ( $v_y$ ) around a rising bubble is 0.36  $v_t$  (Figure 4.5B). This velocity is likely lower than  $v_t$  because the rising bubbles experience extra shear stress from the electrode and other bubbles.

Although the primary motion of the electrolyte is upward, gas bubbles also generate lateral fluid motion, towards and away from the electrode (Figure 4.5C). For increasing hydrogen bubble diameter (50 to 200  $\mu$ m) we observe larger positive and negative lateral velocities, as measured in the  $\mu$ PIV experiments (Figure 4.5D). We can scale the lateral velocities to the relative velocity of rising bubbles, i.e.  $v_x \propto v_t$ , which is derived from the continuity equation (see 4.5.6). A Lagrangian model of a rising bubble with speed

0.36  $v_t$  predicts a lateral velocity of  $v_x \sim 0.085 \cdot v_t$  (see 4.5.6). However, most measured  $v_x$  were smaller than  $0.085 \cdot v_t$ , especially for smaller bubbles, and a log-log fit showed that  $v_x$  scales more like  $d_{\text{bubble}}^{2.32}$ . This could be the result of some bubbles being slightly out of focus plane, or possibly because of other factors (i.e. surface forces) which have a greater impact on smaller bubbles. In any case, we can conclude that larger bubbles create higher lateral velocities, thus stronger convective mixing.



Figure 4.5: A. Change in boundary layer thickness ( $\Delta \delta_{\text{eff}}$ ) for different  $d_{\text{bubble}}$  as observed in FLIM. The datapoints correspond to the detachment events of Figure 4.3 B. Measured velocity of rising H<sub>2</sub> bubbles in 1 M KOH next to an electrode with no forced convection (0 mL min<sup>-1</sup>). The data was fitted to Eq 4.6, scaled with a constant (see 4.5.6 a log-log plot). C. Sketch of a typical flow field after bubble detachment. D. Maximum positive and negative observed  $v_x$  during bubble detachment. The data is compared to the observed velocity of bubbles (0.36 $v_t$ ), the predicted lateral velocity (0.085 $v_t$ ) and power law fit (see 4.5.6 for log-log plot).

However, at equal current density, large bubbles require more time to form than smaller bubbles. A bubble with a diameter of 150 µm contains the same amount of gas as 27 smaller bubbles with a diameter of 50 µm. Consequently, for 50 µm bubbles, the electrolyte is refreshed far more frequently. While  $v_x$  does not directly translate to a mass transport coefficient (k), because it does not include the bubble release frequency and passing bubble events, we can use it for a rough estimate. If we assume that the total convective mixing for bubble release events is proportional to the amount of bubbles and peaks in  $v_x$ , we can indicate the effect of bubble diameter. Because the number of bubbles scales with  $d^{-3}$ , and the lateral velocity scales with  $v_t$  (thus scales with  $d^2$  or  $d^{2.32}$  see 4.5.6), we argue that many smaller bubbles create more mixing than few larger bubbles. This is in agreement with work of Haverkort[8], which revealed that k scales with  $d_{\text{bubble}}^{-0.5}$ .

#### **4.3.4. LIMITATIONS OF μPIV AND FLIM FOR ANALYSING MASS TRANSPORT** Mass transport research is primarily relevant for industrial applications when conducted at high current densities, where large volumes of bubbles are generated. At these higher current densities, bubble coalescence occurs more frequently, significantly enhancing mass transport, as reported in prior studies[8, 16]. Consequently, we explore the limitations of using μPIV and FLIM at higher current densities in this section.

At higher current densities more bubbles can be observed, which are both growing bubbles on the electrode and detached bubbles passing by at a higher frequency (Figure 4.6A). The effect of the wake flow caused by passing bubbles has a significant and frequent impact on the surrounding fluid dynamics, which can be seen in the many regions with elevated velocities (Figure 4.6B). Additionally, the distinct velocity profile around a rising bubble (Figure 4.5C) becomes less common at higher current densities, as the fluid will often need to manoeuvre around a collection of gas bubbles that are on the electrode. We observe that the velocity fields that we measured around "single bubbles" do not exist anymore at >5 mA cm<sup>-2</sup>, which raises concerns about the applicability of mass transport data from micro-electrode experiments to higher current densities.

Figure 4.6C and D show the maximum positive and negative  $v_x$  as a function of current density, where the maximum  $v_x$  was averaged over 25 frames (5 s). The magnitude of  $v_x$  increases with current density, independent of applied forced convection. We believe this increase in  $v_x$  is primarily due to the increasing number of rising bubbles, in addition to having more large (>150 µm) bubbles available at higher current densities. Unfortunately, the large amount of bubbles no longer allowed us to model the mass transport with a continuum model and using our measured velocity field. We can no longer assume that the entire domain is electrolyte. Additionally, some bubbles generate sharp velocity gradients which resulted in numerical instabilities. Hence, the resulting µPIV data is not suitable for our modelling method and will not result in physically correct fields at current densities above 5 mA cm<sup>-2</sup>.

At the same time, FLIM can provide accurate boundary layer thicknesses above 10 mA cm<sup>-2</sup>. We measured ( $\delta_{eff}$ ) up to 16 mA cm<sup>-2</sup> in our static cuvette cell (Figure 4.3), and are able to use FLIM for pH boundary layers up to 50 mA cm<sup>-2</sup> in a flow cell with gas-evolving solid silver plate electrode (see 4.5.7). Previous research by Baumgartner et al.[11] has demonstrated that FLIM can be even used at current densities as high as 100 mA cm<sup>-2</sup> in a CO<sub>2</sub> electrolyzer with gas diffusion electrodes. We believe the FLIM is better capable of capturing the fluid-averaged mass transport at dense bubbly electrodes because 1) it is a more direct measurement of concentration (rather than via a complex velocity field), 2) the tracer is a dissolved dye instead of physical particles, and 3) the upstream concentrations and non-steady effects are included in the direct pH mapping.



Figure 4.6:  $\mu$ PIV investigation at higher current densities A. Images and B. x-velocity fields at higher current densities. C. Maximum observed postive and D. negative  $v_x$  for increasing current densities. The maximum velocities were taken in each frame, and then averaged over 25 frames (5 s). Error bar is standard deviation.

#### **4.4.** CONCLUSIONS

In this work we investigated the microprocesses that drive bubble-induced mass transport at vertical hydrogen-evolving electrodes. We used two optical methods in our investigation: FLIM and  $\mu$ PIV in combination with a mass transport model.

The FLIM experiments revealed that bubble detachment and the resulting wake have the largest role in enhancing mass transport. The  $\mu$ PIV experiments confirmed these observations as the calculated mass transport was highest during bubble detachment. Additionally, we observed that a "single bubble" does not exist, even at low current densities (<5 mA cm<sup>-2</sup>) and small electrodes, since a bubble will always experience wake flow effects of passing bubbles. We also observe that microprocesses of bubble induced mass transport were stronger for larger bubble diameters, but that smaller bubbles together create more mixing.

To conclude, FLIM and  $\mu$ PIV are effective methods for investigating bubble-induced mass transport at the microscale. However, gas bubbles make imaging difficult at higher current densities. We believe combination of  $\mu$ PIV and continuum modelling is not suitable for investigating hydrogen evolving electrodes at atmospheric pressure at current densities above 5 mA cm<sup>-2</sup>. In contrast, FLIM remains a usable technology, even at higher current densities (>50 mA cm<sup>-2</sup>).

## **4.5. SUPPLEMENTARY INFORMATION 4.5.1. Photos of the setup**



Figure S4.1: (Left) Photograph of the setup with 1. µPIV camera 2. Microscope 3. 3D printed holder for the electrolyzer on a movable plate (controlled with joystick) and lens objectives. This holder can be replaced with a 3D holder for a cuvette 4. µPIV Laser camera 5. Halogen lamp (used when setting up and focussing) 6. Spinning disk confocal unit 7. FLIM camera (**Right**) Photograph of the setup during µPIV operation



Figure S4.2: Photos of the electrochemical flow cell used for  $\mu PIV$ 

#### **4.5.2.** μ**PIV** METHOD EXPLANATION

In this section we explain the  $\mu$ PIV method, from taking the images up to obtaining the velocity profile, see Figure S4.3:



Figure S4.3: (Left) Schematic representation of the light path from the laser to the camera. (Right) Schematic step-by-step explanation of PIV

Imaging: The  $\mu$ PIV system was calibrated using LaVision's 50  $\mu$ m calibration plate, which includes mark spacing. When using 10x/0.30 objective, the scale factor is 1.59 pixel  $\mu$ m<sup>-1</sup>. The total image size was 1376 x 1040 pixels<sup>2</sup> or 863 x 652  $\mu$ m<sup>2</sup>. Throughout the experiments, the particles had a diameter of 2-4 pixels. The number of particles in a 128px by 128px interrogation window was around 10. The time interval between a double frame was adjusted so that the displacement of the particles did not exceed 25% of the largest interrogation window. In the validation experiments at 0 mA cm<sup>-2</sup>, a double frame time interval between 2 ms and 90 ms was used. In the other experiments, the time interval was varied between 0.5 ms and 10 ms. In every experiment a video of 100 to 200 double frames was taken (20 - 40 s).

Pre-processing of the double images: The images were pre-processed in the DaVis software in three steps (see Figure S4.4):

- 1. **Masking** To ensure only particles in the fluid were tracked, a geometric mask was applied over the electrode.
- 2. **Subtract time filter** To minimize background noise, the average intensity of each pixel position over all frames (100 to 200 double images) was subtracted from all images.
- 3. **Subtract pixel intensity** Because of lens effects and particles in front and behind the focal plane, small clouds appear. To make sure only particles in focus were tracked, we subtracted between 10 to 25 counts from all pixels. This significantly improved the signal-to-noise ratio.

<u>PIV cross-correlation</u>: The velocity vector fields were calculated with cross-correlation in the DaVis software[36]. This was done in two steps: First a 512 x 512 interrogation window was used with 50% overlap, then an interrogation window of 128 x 128 was used with four passes with a 75%

overlap. The data from the  $512 \times 512$  interrogation window was used to find the best correlation near the predicted vector in the  $128 \times 128$  interrogation windows. After cross-correlation the data was post processed with a 5x5 median filter.



Figure S4.4: µPIV pre-processing steps

#### 4.5.3. COMSOL MODEL EXPLANATION

Here we describe the parameters, equations and boundary conditions used the in COMSOL model. 2D concentration fields were calculated from the velocity fields obtained in the  $\mu$ PIV measurements. Our system is modelled as a water electrolyzer, similar to the FLIM experiments, generating OH<sup>-</sup> at the electrode (Figure S4.5). We acknowledge that these equations strongly simplify a water electrolysis system, and serve only to understand the magnitude of mass transport from the obtained velocity fields from  $\mu$ PIV.



Figure S4.5: Graphical representation of the domain and boundary conditions of the COMSOL model
Model Geometry: The model has a rectangular geometry, which matches the visualized area in the PIV experiments, which was 582.2  $\mu$ m by 782.9  $\mu$ m. The model uses a triangular physics controlled "extra fine" mesh. All meshes were generated automatically by COMSOL. The "extremely fine" mesh did not yield significantly different results, hence we used the coarser mesh to reduce computation time.

<u>Material</u>: We model the transport of OH<sup>-</sup> in water with diffusion coefficient ( $D_{OH}$ ) 5.27 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup> (Source: Aqion.de).

Governing equations & boundary conditions: The transport of OH<sup>-</sup> is calculated with the "Transport of diluted species" module of COMSOL:

$$\frac{\partial N_{OH}}{\partial y} + \frac{\partial N_{OH}}{\partial x} + v_y \frac{\partial c_{OH}}{\partial y} + v_x \frac{\partial c_{OH}}{\partial x} = R_{OH}$$
(S4.1)

Convective transport is calculated with the experimentally obtained velocity field. As initial value for the calculations, we used  $c_{OH} = 0$ . The left boundary is a constant concentration ( $c_{OH}(x=0) = 4$  mmol L<sup>-1</sup>) to mimic the electrode from the FLIM measurements in Figure 4.3. On the right side, a constant concentration boundary condition with the bulk concentration was used ( $c_{OH}(x=L) = 0$ ). The top and bottom have a periodic boundary condition (Figure S4.5).

Importing the  $\mu$ PIV velocity field: The velocity fields were exported from the DaVis PIV-software as x-coordinate, y-coordinate,  $v_x$  and  $v_y$ . Before loading the data into COMSOL, the outliers of the velocity field are removed. The vectors with the highest and lowest 1%  $v_x$  values were removed, because we observed the  $\mu$ PIV experiments would sometimes result into few incorrectly large velocity vectors, especially near the electrode and the boundaries of the image. After processing the data, the velocity vectors are imported to COMSOL. These velocity vectors were converted into a 2D velocity field with linear interpolation in the software.

Post-processing of the model results: A 2D concentration field was obtained after running the model. The boundary layer was extracted by plotting a contour line at 5% of 4 mmol L<sup>-1</sup>, which was exported as x- and y-coordinates. Since the y-coordinates were spaced irregularly, we calculated the effective boundary layer thickness ( $\delta_{eff}$ ) with a discretized version of Eq 4.5 (see derivation in next section):

$$\delta_{\rm eff} = L \left( \sum_{i=1}^{N} \frac{L_i}{\delta_i} \right)^{-1}$$
(S4.2)

Here  $\delta_{\text{eff}}$  is the effective boundary layer thickness, *L* is the total y-length of the boundary layer profile, *L<sub>i</sub>* is the y-distance between two datapoints and  $\delta_i$  is the boundary layer thickness at that datapoint.

Derivation of effective boundary layer thickness ( $\delta_{eff}$ ): To derive the equation for  $\delta_{eff}$ , we assumed that inside the mass-transport boundary layer all mass transport is through diffusion. At a given height *y* along the electrode, the mass flux will be given by Fick's law:

$$N(y) = -D\left(\frac{dc}{dx}\right) \cong -D\frac{\left(c_{\text{bulk}} - c(x=0)\right)}{\delta(y)} = D\frac{c(x=0)}{\delta(y)}$$
(S4.3)

Here, N(y) is the flux at point y, D is the diffusion coefficient, c is the concentration,  $c_{\text{bulk}}$  is the bulk concentration outside the boundary layer (which is 0) and  $\delta(y)$  is the boundary layer thickness at point y. If we want to calculate the average mass flux ( $N_{\text{avg}}$ ) along an electrode with length L, we can integrate the Eq S4.3:

$$N_{avg} = \frac{\int_0^L N(y) \, dy}{L} = \frac{Dc(x=0) \int_0^L \frac{1}{\delta(y)} \, dy}{L}$$
(S4.4)

If we discretize this integral, the equation becomes:

$$N_{\text{avg}} = \frac{Dc(x=0)\sum_{i=1}^{N} \frac{L_i}{\delta_i}}{L}$$
(S4.5)

Here  $\delta_i$  is the boundary layer thickness for point *i* and  $L_i$  is the distance until the next datapoint. If we now rewrite  $N_{\text{avg}}$  like Fick's law, we get the following equation:

$$N_{\rm avg} = D \frac{c(x=0)}{\delta_{\rm eff}}$$
(S4.6)

By then combining Eq S4.5 and S4.6 we get:

$$\frac{1}{\delta_{\text{eff}}} = \frac{\sum_{i=1}^{N} \frac{L_i}{\delta_i}}{L} \to \delta_{\text{eff}} = L \left(\sum_{i=1}^{N} \frac{L_i}{\delta_i}\right)^{-1}$$
(S4.7)

# 4.5.4. OH<sup>-</sup> CONCENTRATIONS DURING FLIM EXPERIMENTS

See figure S4.6 on next page.

### 4.5.5. µPIV METHOD VALIDATION

Here we validate our approach to use  $\mu$ PIV for mass transport research, i.e. to show that the fluctuations originating from the forced convection have minimum impact on the resulting concentration plots. This way we can confirm that our method only sees the effect of gas bubbles, and is not influenced significantly by the pumping of electrolyte. The flow needs to fulfill the following requirements:

- A relatively stable, unidirectional flow ( $v_y * v_x, \partial v_y / \partial y = \text{small}$ ). This will allow us to distinguish the effects from gas bubbles, from deviations in the velocity due to non-steady flow.
- The flowrate needs to be large enough avoid heating up from the laser light source, which could result in natural convection.

Figure S4.7A and B show an image taken and the corresponding  $v_x$  velocity field, which shows that the flow is almost unidirectional, but still has small (<0.1 mm s<sup>-1</sup>) fluctuations in the  $v_x$ . Figure S4.7C and D show the  $v_x$  and  $v_y$  over the width of the frame, averaged over the height of the frame and over 25 frames (5 s). The beginning of a parabolic flow profile can be seen, which increases linearly with flowrate, indicating that the flow is fully developed.

However at 1 mL min<sup>-1</sup> we observed small effects of natural convection due to heating from the light source. We therefore chose to do all bubble induced mass transport experiments at flowrates of 2 mL min<sup>-1</sup> or higher. The  $v_x$  is around 0 mm s<sup>-1</sup>, but the deviations increase at higher flowrates. We decided to not measure at flowrates above 5 mL min<sup>-1</sup> to minimize effects of forced convection on the concentration plots. Figure S4.7E shows the calculated concentration field after implementing the velocity profile from Figure S4.7B. An almost linear profile can be observed, indicating that mass transport is mostly by diffusion, hence the small fluctuations in  $v_x$  do not significantly influence the calculated boundary layer thickness. Figure S4.7F shows that the boundary layer thickness over 25 frames (5 s) is not strongly influenced by flow fluctuations, and is at least an order of magnitude smaller than the effect of gas bubbles.

Hence we confirm that we developed a system that can be used to investigate the effect of gas bubble dynamics on mass transport, without being affected by the small fluctuations in the flow due to forced convection or heating.



Figure S4.6:  $c_{OH}$  averaged over the length of the electrode vs *x*, for various timestamps, and 2D  $c_{OH}$  plots at various timestamps during the FLIM experiment of Figure 4.3. The red dashed line in the  $c_{OH}$  vs *x* plot indicates the cut-off point of the boundary layer. In the 2D concentration plots, the white and red line are the electrode surface and boundary layer cut-off respectively.

# 4.5.6. EFFECT OF BUBBLE DIAMETER ON FLUID VELOCITIES

To find the relation between the velocity of the bubble  $(v_t)$ , and the lateral velocity of the fluid  $(v_x)$  we perform order-1 scaling on the 2D-continuity equation:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \tag{S4.8}$$

If we nondimensionalize Eq S4.8, the equation becomes:

$$\frac{[v_x]}{[x]}\frac{\partial v_x^*}{\partial x^*} + \frac{\partial v_y^*}{\partial y^*} = 0$$
(S4.9)



Figure S4.7: A.  $\mu$ PIV image of the electrode with a 5 mL min<sup>-1</sup> flowrate and no applied current (0 mA cm<sup>-2</sup>) B. Corresponding velocity field. Streamlines indicate the flow direction, the color contour is the velocity component in the x-direction C. y-velocity and D. x-velocity over the width of the image at different flowrates, averaged over 25 frames (5 s), error bar is std deviation. E. Resolved concentration profile after implementing the flowfield of B in the mass transport model, dashed red line indicates the boundary layer E  $1/\delta_{\rm eff}$  when applying no current, compared to a system with only diffusion (all velocities in the model are set to 0).

Here \* indicates the nondimensional variable, and the square brackets indicate the length scale of the velocity profile or the magnitude of the velocity. We then apply O(1) scaling.

$$\frac{[v_x]}{[x]} \quad \frac{[v_y]}{[y]} \tag{S4.10}$$

In our measurements, we observed that velocity profiles are present about one  $d_{\text{bubble}}$  around the bubble, therefore [*x*] and [*y*] are both proportional to  $d_{\text{bubble}}$ . The y-velocity is proportional to the terminal velocity. Thus:

$$[v_y] = v_t \quad [x] = [y] = d_{\text{bubble}} \tag{S4.11}$$

And:

$$[v_x] \sim v_t \tag{S4.12}$$

We also developed a 3D continuum CFD model in COMSOL to simulate a gas bubble rising near a wall and to find the scale of the lateral velocity  $[v_x]$ . To simplify the model, we used a Lagrangian reference frame (i.e. the model follows the bubble, so the bubble appears stationary while the surrounding fluid and wall are moving downwards). The bubble was modelled as a solid sphere. The gap between the bubble and the wall and the bubble was set to  $0.1d_{bubble}$  and the velocity of the wall and fluid are  $-0.36v_t$ . Figure S4.8B shows a typical velocity profile calculated with the model, the shape closely resembles the observed profiles in µPIV. Figure S4.8C shows that the model finds lateral velocities of around  $0.085v_t$ .



Figure S4.8: A. log-log plot of Figure 4.5 B. Sketch of the Lagrangian model around a rising bubble, and examples of x and y-velocity profiles for a bubble with dbubble of 80  $\mu$ m C. Comparison of modelled velocities to 0.085  $v_t$  D. log-log plot of Figure 4.5D.



# 4.5.7. FLIM Experiments at higher current densities

Figure S4.9: A. 2D-pH resolved images with FLIM at increasing current densities. A CO<sub>2</sub> electrolyzer catholyte compartment is visualized, with the setup from Baumgartner et al. where the gas compartment is removed[11]. The experiments are done on a Ag cathode in 1 M KHCO<sub>3</sub> saturated with CO<sub>2</sub> under a flowrate of 1.4 mL min<sup>-1</sup> (*Re* = 8). It can be seen, that even if during a of gas evolution at 50 mA cm<sup>-2</sup> a local OH boundary layer is still visible and can be resolved. B. Cross-sectional diagram of the setup used. All images in A are taken in the middle of the cell (2).

# **4.6.** SUPPLEMENTARY VIDEOS



Video S4.10: Video of a forming OH<sup>-</sup> boundary layer at a H<sub>2</sub> evolving Pt wire electrode in 0.2 M K<sub>2</sub>SO<sub>4</sub>. Corresponds to Figure 4.3.

https://www.youtube.com/watch/v6-9Vy2YgXM



Video S4.11: Video at a H<sub>2</sub> evolving Ni plate electrode (1 M KOH, 2.5 mA cm<sup>-2</sup>, 5 mL min<sup>-1</sup> flowrate). Corresponds to Figure 4.4A. https://www.youtube.com/watch/Kc\_47FWNBts



Video S4.12: Video of the lateral velocity ( $v_x$ ) at a H<sub>2</sub> evolving Ni plate electrode (1 M KOH, 2.5 mA cm<sup>-2</sup>, 5 mL  $min^{-1}$  flowrate). Corresponds to Figure 4.4B. https://www.youtube.com/watch/tnHVfxtHZZw

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# 5

# CO<sub>2</sub> ELECTROLYSIS UNDER PRESSURE PULSED FLOW

# **Pressure pulsed flow**





This chapter has been submitted for publication as "Pressure-pulsed flow triples mass transport in aqueous CO<sub>2</sub> electrolysis" by Jorrit Bleeker, Lisanne C. Bakker, Sue S.J. van Deursen, Timo J.J.M. van Overveld, Katie M.R. Lawrence, Isabell Bagemihl, Giacomo Lastrucci, Duco Bosma, Christiaan V. Schinkel, Evert C. Wagner, J. Ruud van Ommen, David A. Vermaas.

# **Context & Scale**

The energy transition requires moving away from fossil fuels to renewable electricity. However, sectors such as long-distance transport and plastic manufacturing need carbon-based chemicals. These sectors are responsible for 100's millions tons of chemicals per year, which is equivalent to 10-20% of CO<sub>2</sub> emissions. Electrochemical CO<sub>2</sub> reduction presents a promising alternative, enabling production using only CO<sub>2</sub>, water, and renewable electricity. To make an impact on the climate, CO<sub>2</sub> electrolysis needs to be urgently developed to a scalable design.

Here, we presents a potential breakthrough: a liquid aqueous  $CO_2$  electrolyzer operating under pressure-pulsed flow, improving mass transport with a cheap vibratory pump. This method achieves current densities of 87 mA cm<sup>-2</sup>—an order of magnitude higher than typical aqueous systems. We use high-speed imaging to show that a liquid-fed  $CO_2$  system can attain even higher current densities, making it a viable alternative to gas-fed  $CO_2$ electrolyzers.

#### Summary

Electrochemical CO<sub>2</sub> reduction (CO<sub>2</sub>R) is a promising technology enabling carbon recycling and energy storage. CO<sub>2</sub>R in water has advantages over gas-fed CO<sub>2</sub>R electrolyzers, such as avoiding salt formation or needing water control, though it achieves lower current densities. In this work, we improve the mass transport in an aqueous CO<sub>2</sub> electrolyzer by applying fast pressure pulses (50 Hz, 1.2 bar) with a vibratory pump typically found in coffee machines. We demonstrate a limiting current density of 87 mA cm<sup>-2</sup> towards CO<sub>2</sub>R products, which is almost three times higher than for a system without pulses. The current density can be further increased by leveraging the peak-to-peak pressure amplitude or pump frequency, as shown through particle image velocimetry (PIV) and an order-ofmagnitude scaling analysis. Although challenges remain, such as pump energy consumption, contamination and heating, and pressure wave damping, the pressure-pulsed concept makes aqueous CO<sub>2</sub>R a viable alternative for gas-fed electrolyzers.

# **5.1.** INTRODUCTION

The electrochemical reduction of  $CO_2$  ( $CO_2R$ ) is a promising technology that uses renewable electricity to convert  $CO_2$  and water into fuels and chemicals, enabling carbon recycling, energy storage, and climate change mitigation[1–3]. In  $CO_2R$ ,  $CO_2$  is converted at the cathode into products such as CO,  $C_2H_4$  and formic acid[4]. Hydrogen is an undesirable by-product, and its reaction rate increases when the mass transport of  $CO_2$ to the electrode is insufficient[5, 6] or the catalyst is contaminated[7, 8].

To achieve higher current densities, attention has shifted towards gas-fed reactors with gas-diffusion electrodes (GDE) and membrane electrode assemblies (MEA)[3, 9–12]. With these technical features,  $CO_2R$  can reach and sustain industrially relevant current densities (>300 mA cm<sup>-2</sup>, >1000 hrs) and is being scaled up in start-up companies[13, 14]. However, gas-fed electrolyzers still have problems with stability[15, 16], control of water[17, 18] and salt formation[19]. In addition to the aforementioned challenges, these systems require gaseous  $CO_2$ . If the  $CO_2$  source is an environmental capture system, such as direct air capture with alkaline[20, 21] or amine solutions[21, 22], the  $CO_2$  will first need to be removed from the capture liquid (Figure 5.1A)[23]. In this removal step, the vacuum pumps, compressors and de-humidifiers require 10 to 35% of the energy consumption of a current state-of-the-art  $CO_2$  electrolyzer[21, 24](see 5.5.1 for calculation).



Figure 5.1: A. Schematic drawing of an integrated  $CO_2$  capture and conversion process with a gas-fed electrolyzer. B. Schematic drawing of an integrated  $CO_2$  capture and conversion system with an aqueous  $CO_2$  electrolyzer. The Dissolved Inorganic Carbon (DIC) balancing step is required to convert some of the  $CO_2$  capture solution into dissolved  $CO_2$ 

Aqueous  $CO_2R$  can avoid these costs by directly converting dissolved  $CO_2$  from capture solutions, which reduces the process steps and has potential to simplify the process significantly[22] (Figure 5.1B). Omission of the dissolved  $CO_2$  extraction steps results in lower required capital investments[22], although a balancing step (e.g. by adding an acid) might still be required to create dissolved  $CO_2$  from bicarbonates. Unfortunately, aqueous  $CO_2R$  suffers from low limiting current densities towards  $CO_2$ -based products. In typical electrolyzers, the limiting current densities are an order of magnitude lower compared to GDE-based systems (5-10 mA cm<sup>-2</sup> vs 100-400 mA cm<sup>-2</sup>)[25]. The low limiting current densities in aqueous  $CO_2R$  are a result off depleting  $CO_2$  concentration at the cathode surface, which is caused by the low  $CO_2$  solubility in water and poor mass transport in traditional H-cells and traditional flow-by cells.

Two common approaches for increasing the limiting current density in aqueous  $CO_2R$  are increasing the  $CO_2$  concentration and using in-situ conversion of bicarbonate to  $CO_2$  (e.g. with a bipolar membrane). The  $CO_2$  concentration can be increased by increasing the pressure[26–28], supersaturation of  $CO_2$  in the electrolyte[29], addition of amines[22, 30, 31] or by using organic electrolytes which have a higher  $CO_2$  solubility[32, 33]. Despite substantial work on these approaches, the industrial goals for current density, cell voltage, faradaic efficiency, scalability and lifetime are not fully met yet[34].

A less studied avenue is to leverage gas bubble motion to increase the mass transport of CO<sub>2</sub> from the bulk electrolyte towards the cathode surface. Nano-structured catalysts can break up the diffusion boundary layer through bubble-induced mass transport and obtain a 3-fold increase in current density compared to a flat electrode[6, 35, 36]. Similarly, in gas-liquid microfluidic devices an artificially small diffusion boundary layer can be created, which could give a 1 to 1.5 order of magnitude increase in current density compared to a liquid system[37]. The effectivity of reducing the diffusion boundary layer thickness to achieve high current densities has been confirmed by Wen et al., who obtained current densities of >1000 mA cm<sup>-2</sup> in an exsolution-induced flow cell[38], with a calculated boundary layer thickness of <1.5  $\mu$ m. While effective, these three approaches (nano-structured catalysts, leverage of microfluidics, and exsolution-induced flow cells) require complex reactor and electrode design.

An alternative method for reducing the boundary layer thickness is operating under oscillatory flow conditions (Figure 5.2A). Here, oscillations in the electrolyte flow are induced with a piston or pulsating pump. These oscillations in the flow rate cause vortices in the electrolyte. The vortices create flow perpendicular to the electrode, instead of mainly unidirectional flow parallel to the electrode surface[39]. Oscillatory flow has been successfully applied in electrodialysis[40], redox flow batteries[41] and electrochemical reactors[39, 42]. The oscillation frequencies applied in these studies were between 0.2-3 Hz, and resulted in a 2x[39, 40] to 5x[42] higher limiting current density compared to a steady flow.

In this work, we apply a pressure pulsed flow to increase the limiting current density  $(j_{lim})$  in aqueous CO<sub>2</sub>R. Similar to an oscillatory flow, pressure-pulsed flow induces pressure fluctuations, but at a higher frequency (Figure 5.2B). We create 50 Hz oscillations in the pressure, in which the pressure fluctuates between 1 and 2.2 bar, with a cheap (~18 euro) vibratory pump, typically used in household coffee machines. We experimentally evaluate the mass transport by measuring the limiting current density on a commercial silver mesh cathode, and compare this to a system where pressure dampers are installed. Additionally, the mass transport mechanisms are further studied with high-speed imaging and particle image velocimetry (PIV). Through an order-of-magnitude scaling approach, we conclude that both vibrating bubbles and multidirectional oscillatory flow contribute to enhancing the CO<sub>2</sub>R. Finally, we will evaluate the scalability of an aqueous pressure-pulsed CO<sub>2</sub>R system and discuss three possible issues.

# 5.2. RESULTS

#### 5.2.1. GENERATION AND CHARACTERIZATION OF PRESSURE PULSED FLOW

To ensure adequate mass transport for aqueous  $CO_2R$ , we generate pressure pulses that oscillate the fluid and cause gas bubbles to vibrate. Our vibratory pump, comprises a diode, a spool, and a magnetic piston (Figure 5.2C)[43]. When connected to an AC grid (50 Hz, 220V), the diode converts the electrical signal into a half-wave rectified sine. This creates a periodic electric field in the spool, which moves the piston. As a result, the piston generates 50 pressure pulses per second with an amplitude of 1.5 bar and a flow rate of 530 mL min<sup>-1</sup> (average velocity of 8.9 mm s<sup>-1</sup> in our cell).

However, the pressure waves before and after the electrolyzer were more complex than a half-wave rectified sine (Figure 5.2D). We hypothesize that these extra peaks in the pressure wave are not generated by the pump, but instead result from reflections and vibration in the electrolyzer (see 5.5.2). To understand the effects of pressure pulses on the  $CO_2$  electrolyzer, we also created a reference case where we damped out the pressure waves with pressure dampers (Figure 5.2D). Here the pressure amplitude reduced significantly, but the flow rate remained the same (see 5.5.3).

To characterize the shapes and waveforms, we introduce the following parameters to describe the pressure waves (Figure 5.2E), which are all applied on datasets of >500 pressure waves (i.e. >10 s of data):

- Pavg Time-averaged pressure for each dataset
- P<sub>PP</sub> Peak to peak pressure, P<sub>peak</sub> P<sub>min</sub>, averaged over all pressure waves
- $\chi$  Relative expansion,  $P_{\text{peak}}/P_{\text{min}}$ , averaged over all pressure waves.  $\chi$  expresses the ratio of volume change of gas bubbles (according to the ideal gas law) during the pressure pulse.

Figure 5.2F shows  $P_{PP}$  for the pressure pulsed and damped CO<sub>2</sub> electrolysis experiments, averaged over 4 pressure sensors and 40 min of pressure data. The dampers are effective at reducing the  $P_{PP}$  by 70-80%, and will be a useful comparison case to study the effect of pressure pulses on mass transport. The difference is even larger in  $\chi$ , 2-2.2 for pressure pulsed flow and 1.2-1.3 for damped flow, while the  $P_{avg}$  is similar for both pulsed flow and damped flow (5.5.4).



Figure 5.2: A. Hypothesized mixing behaviour during oscillatory flow B. Hypothesized mixing behaviour during pressure pulsed flow C. Diagram with the workings of a vibratory pump D. Pressure waves at the inlet of the cathode channel in the electrolyzer with no applied current (Pulsed) and when two pressure dampers are installed (Damped) E. Schematic presentation of the peak pressure ( $P_{\text{peak}}$ ), minimum pressure ( $P_{\text{min}}$ ), time averaged pressure ( $P_{\text{avg}}$ ) and the peak to peak pressure ( $P_{\text{PP}}$ ) F.  $P_{\text{PP}}$  at the inlet of the cathode for different current densities for pressure pulses and damped pulses

## **5.2.2.** EFFECT OF FAST PRESSURE PULSES ON CO<sub>2</sub>R PERFORMANCE

To express the performance of the pressure pulsed aqueous  $CO_2$  electrolyzer, we use the limiting current density ( $j_{lim}$ ) – the maximum obtained partial current density of  $CO_2R$ , at which the  $CO_2$  concentration at the cathode surface is assumed to approach zero.

Figure 5.3A and B show the faradaic efficiency after 10 minutes of electrolysis for a pressure pulsed and a damped system under constant current. Up to 50 mA cm<sup>-2</sup>, the faradaic efficiencies are very similar for the two flow types. CO is the major product with 60-70% faradaic efficiency, while less than 10% of the current is used for H<sub>2</sub>. We note that this partial current density for CO<sub>2</sub>R is already higher than for typical H-cells (5-10 mA cm<sup>-2</sup>)[25], which is likely due to the large flow rate in our system. At higher current densities, the FE<sub>CO</sub> for the damped system (Figure 5.3B) significantly decreases, indicating strong CO<sub>2</sub> mass transport limitations. At the same time, the pulsed (Figure 5.3A) system still performs well (FE<sub>CO</sub> > 50%) at 130 mA cm<sup>-2</sup>. Even at 200 mA cm<sup>-2</sup>, approximately half of the observed products are CO<sub>2</sub>R products, including small amounts (FE<sub>i</sub> < 5%) of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CHOO<sup>-</sup>, and EtOH.

The total FE was close to 80% at both the anode and cathode. The remaining 20% of products is lost because catholyte and anolyte are mixed in the same container. This leads to faradaic losses, as some  $O_2$ ,  $CO_2R$  products and  $H_2$  are recycled and consumed at the electrodes instead of producing new products. We expect the actual faradaic efficiency towards  $CO_2R$  products to be slightly higher when catholyte and anolyte are separated. Figure 5.3C compares the partial current densities of a pressure pulsed and damped system. To express the consumption of  $CO_2$ , while taking care of the number of electrons per  $CO_2$  molecule, we introduce the equivalent CO partial current ( $j_{CO-eq}$ ), which is the current as if all products were CO:

$$j_{\rm CO-eq} = j_{\rm CO} + \frac{1}{4} j_{\rm CH_4} + \frac{1}{3} j_{\rm C_2H_4} + j_{\rm CHOO^-} + \frac{1}{3} j_{\rm EtOH}$$
(5.1)

Here  $j_i$  is the current density towards a specific CO<sub>2</sub>R product, which is multiplied with the ratio of electrons compared to CO ( $n_{\rm CO}/n_i$ , where n is the number of electrons per molecule of product). Under pressure pulsed flow, a maximum  $j_{\rm CO-eq}$  of is 87 mA cm<sup>-2</sup> was obtained, compared to 33 mA cm<sup>-2</sup> when the flow is damped. Hence, the fast pressure pulses increase the limiting current density of CO<sub>2</sub>R products by 2.6 times. Because the flow rate and  $P_{\rm avg}$  for the flow regimes are the same, we can conclude that pressure pulses are the main cause of increased CO<sub>2</sub> mass transport.

A partial current density of 87 mA cm<sup>-2</sup> is among the highest reported for aqueous  $CO_2R[25]$ . To compare our work to other aqueous  $CO_2R$  works, the  $j_{CO-eq}$  is plotted against the product of FE and voltage efficiency (VE) (Figure 5.3D). The FE-VE can be used to show the energy efficiency of an electrolyzer.

H-cell based systems can reach a high FE-VE (25-50%), but typically only reach  $j_{\text{CO-eq}}$  of 5-10 mA cm<sup>-2</sup> (ref [28, 44–50]). An exception to this is the work of Burdyny et al.[6], which utilizes gold nanostructured electrodes to promote gas-bubble induced mass transport to achieve a  $j_{\text{CO-eq}}$  of ~55 mA cm<sup>-2</sup>. Systems operating under higher pressures (3-10 bar)[28, 29, 48] could alleviate mass transport limitations as the CO<sub>2</sub> solubility linearly increases with pressure. However, only Lamaison et al.[48] reported high partial current densities (up to 287 mA cm<sup>-2</sup>) at 10 bar. A direct bicarbonate electrolysis based system[8,

51] can reach similar or slightly higher current densities to our system ( $j_{CO-eq}$  of 45-127 mA cm<sup>-2</sup>), but requires a bipolar membrane and therefore a higher operating voltage. The exsolution based system[38] remains the best reported aqueous CO<sub>2</sub>R systems to date, with both high currents (~1000 mA cm<sup>-2</sup>) and a good energy efficiency. These high current densities were achieved with a flow-through electrode in combination with a CO<sub>2</sub> supersaturated electrolyte.

The high  $j_{CO-eq}$  in the exsolution-based system was achieved when combining methods to increase the CO<sub>2</sub> concentration and mass transport. In that line of reasoning, pressure pulsed CO<sub>2</sub> electrolysis can further expand its potential when combined with CO<sub>2</sub> supersaturation or pressurization. We believe that aqueous systems with such combined enhanced CO<sub>2</sub> concentration and mass transport could reach similar current densities as in gas-fed processes, while keeping the benefits of an aqueous process.



Figure 5.3: Faradaic efficiency against total current density under A. Pressure pulsed flow and B. Damped flow, for comparison  $FE_{O_2}$  at the anode is also shown. C. Partial current density as if all products were CO ( $j_{CO-eq}$ ) against total current density, also displayed as molar CO<sub>2</sub> consumption on the right axis. Operating conditions: Ag mesh cathode, IrOx anode, 20 °C, 0.5 M KHCO<sub>3</sub> saturated with 1 atm CO<sub>2</sub>. All experiments were performed with duplicates, error bars are the standard error. The cathode voltage during the CO<sub>2</sub>R experiments is shown in 5.5.5. D. Literature comparison of energy efficiency (expressed as FE·VE) and limiting current density ( $j_{CO-eq}$ ). See 5.5.6 for data and references.

#### **5.2.3.** The mass transport mechanisms of pressure pulsed flow

To understand the effectivity of pressure pulsed flow for increasing the limiting current density ( $j_{lim}$ ), we estimate the diffusion boundary layer thickness. With the assumption that the current density is only limited by mass transport of CO<sub>2</sub> towards the cathode,  $j_{lim}$  can be expressed as follows:

$$\frac{j_{\rm lim}}{nF} = \frac{D_{\rm CO_2} C^*_{\rm CO_2}}{\delta} \tag{5.2}$$

Here *n* is the amount of electrons per CO<sub>2</sub>, *F* is the Faraday constant,  $D_{CO_2}$  is the diffusion coefficient of CO<sub>2</sub>,  $C_{CO_2}^*$  is the bulk concentration of CO<sub>2</sub> and  $\delta$  the diffusion boundary layer thickness. Using a  $j_{lim}$  of 87 mA cm<sup>-2</sup> in eq. 5.2, we calculate the diffusion boundary layer thickness to be approximately 14.5 µm, for all temperatures between 15 – 30 °C, see Table 5.1. For damped pressure pulses, the estimated  $\delta$  is 38 µm.

Table 5.1: Calculation of the diffusion boundary layer thickness ( $\delta$ ) for different temperatures at 1 atm of CO<sub>2</sub> for a  $j_{\text{lim}}$  of 87 mA cm<sup>-2</sup> (Pulsed) and 33 mA cm<sup>-2</sup> (Damped). Solubility and diffusion data from CRC Handbook[52]

$T(^{\circ}C)$	$C^*_{\rm CO_2} \ ({\rm mol} \ {\rm m}^{-3})$	$D_{\rm CO_2}~({\rm m^2~s^{-1}})$	$\delta_{ m Pulsed}$ ( $\mu$ m)	$\delta_{ m Damped}$ ( $\mu$ m)
15	45.6	$1.45\cdot 10^{-9}$	14.6	38.6
20	39.2	$1.67\cdot 10^{-9}$	14.5	38.3
25	34.1	$1.91\cdot 10^{-9}$	14.5	38.1
30	30.0	$2.17\cdot 10^{-9}$	14.5	38.1

We identified two mixing mechanisms by studying the electrolyzer with high-speed imaging and Particle Imaging Velocimetry (PIV): the vibration of gas bubbles caused by fast pressure changes (Figure 5.4A) and multidirectional oscillatory flow (Figure 5.4D).

#### VIBRATING GAS BUBBLES

In the high-speed videos (see videos in section 5.6) we observed growing and shrinking gas bubbles on the electrode (Figure 5.4A). These vibrations were caused by the rapid pressure changes during a pulse (1 to 2.5 bar, Figure 5.4B). Figure 5.4C shows the gas bubbles at different stages of the pressure pulse, which drive fluid in all directions by growing and shrinking[53]. Notably, some gas bubbles also move inside the porous mesh electrode during the peak of the pulse, thereby pulling fluid towards the electrode. We believe these vibrations enhance the mixing of electrolyte from the bulk to the electrode, thereby sustaining high local  $CO_2$  concentrations. The volume of the bubbles scales with pressure according to the ideal gas law:

$$\frac{V_{\min}}{V_{\text{peak}}} = \frac{d_{\min}^3}{d_{\text{peak}}^3} = \frac{P_{\text{peak}}}{P_{\min}} = \chi$$
(5.3)

Where  $V_i$ , and  $d_i$  are the bubble volume and the bubble diameter at the peak and minimum of a pressure wave. The convective mass transport around the bubbles (quantified in mass transfer coefficient  $k_{\text{Bubble}}$ , in m s<sup>-1</sup>) scales with the local velocity perpendicular to the electrode ( $v_x$ ) which at the bubble-liquid interface is equal to dd/dt:

$$k_{\text{Bubble}} \propto v_{\text{x,Bubble}} \sim \frac{\mathrm{d}d}{\mathrm{d}t} \sim \frac{d_{\text{peak}} - d_{\min}}{t_{\text{peak}}} \sim \frac{d_{\min}}{0.1/f} \left(\chi^{-1/3} - 1\right)$$
 (5.4)

Here  $t_{\text{peak}}$  is the time between a minimum and maximum pressure, which is about 0.1/*f* in our experiments, where *f* is the frequency of the pump in s<sup>-1</sup>. Hence, when comparing two systems with gas bubbles in similar amount and size, the mass transport due to oscillating bubbles scales with the ratio between  $f(\chi^{-1/3} - 1)$  in the pulsed flow and the damped flow.



Figure 5.4: Mass transport mechanisms in pressure pulsed  $CO_2 R A$ . Growing and shrinking gas bubbles due to the pressure changes. Typical bubble diameters ( $d_{bubble}$ ) are 50-500 µm,  $\delta_{mass}$  is the mass transport boundary layer B. Pressure wave during high-speed imaging averaged over 350 pulses, points correspond to images in C; C. Image of the Ag mesh during a pressure pulse, a gas bubble is moving in and out of the pore, scalebar is 200 µm D. Mixing due to the multidirectional oscillatory flow and circulations. E. Average fluid velocity perpendicular to the electrode ( $v_x$ ), obtained with PIV and averaged over 10 pulses. The time on the horizontal axis corresponds to that in B. For more information, see 5.5.7 F. Comparison of the pressure gradient measured at the inlet of the electrolyzer( $dP_{Inlet}/dt$ ) to  $v_x$  at the electrode, see 5.5.8 for  $dP_{Outlet}/dt$ . See 5.5.9 for PIV results of the damped case.

## MULTIDIRECTIONAL OSCILLATORY FLOW

The inlet of the flow channel is inclined relative to the electrode's surface (Figure 5.6B). This, in combination with the relatively high flow rate and oscillations, creates a complex transient flow with velocities components in all three dimensions (Figure 5.4D), which improves the mass transport. To gain a better understanding of the mixing behaviour, the velocity field near the cathode was visualized with PIV (see 5.5.7). We did not observe turbulence but rather multiple periodic circulations within the flow, which matches the regime of the time-averaged Reynolds number (Re = 10-100). Figure 5.4E shows the  $v_x$  during a pressure pulse (see 5.5.8 for  $v_y$ ). The velocity profile does not

significantly change while varying the distance from the electrode (0.05, 0.1 and 0.25 mm), which indicates bulk motion of fluid towards the electrode and likely fluid moving through the electrode pores.

The mixing due to oscillatory flow scales with  $v_x$ , which we hypothesize to scale with dP/dt. This is observed in Figure 5.4F, where the largest peaks in pressure change (dP/dt), in the first 4 ms of the wave, have a similar profile as  $v_x$ . Our hypothesis for the relation between  $v_x$  and dP/dt is further supported by estimating the pressure gradient dP/dy due to oscillations, which is an order of magnitude larger than the pressure drop due to mean flow in our system (see 5.5.10 for calculation). Hence, the forces on the water caused by oscillations are dominating, compared to the forces caused by mean flow. Using this scaling analysis, we estimate the mass transfer coefficient  $k_{Osc}$  (in m s<sup>-1</sup>):

$$k_{\rm Osc} \propto v_{\rm x, Osc} \propto \frac{\mathrm{d}P}{\mathrm{d}t} \sim \frac{P_{\rm PP}}{0.1/f}$$
 (5.5)

The mass transport due to oscillations scales with  $P_{\text{PP}}$ , which we also observed with a statistical analysis (5.5.11). Hence, when comparing two systems, the mass transport due to oscillatory flow will scale with  $f \cdot P_{\text{PP}}$  values of the two experiments.

# **COMPARISON BETWEEN PULSED & DAMPED FLOW**

The flow properties of the pulsed and damped  $CO_2R$  experiments are compared in Table 5.2. The ratios of ( $\chi^{-1/3} - 1$ ) (2.2 to 3.9) and  $P_{PP}$  (2.5 to 4.5) are in the same order of magnitude as the increase in  $j_{CO-eq}$  (or  $CO_2$  mass transport towards the electrode). We conclude that both mechanisms could cause the enhanced mass transport. The exact ratio of contribution to the mass transport of these two processes will depend on the gas bubble coverage on the electrode.

Table 5.2: Comparison of the scaling factors for bubble oscillation induced mixing ( $\chi^{-1/3} - 1$ ) and oscillatory flow induced mixing ( $P_{PP}$ ) to the CO<sub>2</sub> mass transport, expressed as  $j_{CO-eq}$ . f = 50 in both flow regimes.

	$(\chi^{-1/3} - 1)$ (-)	$P_{\rm PP}$ (bar)	$j_{\rm CO-eq}$ (mA cm <sup>-2</sup> )
Pulsed flow	-0.26 to -0.30 (χ: 2-2.2)	1 to 1.2	87
Damped flow	-0.06 to -0.11 ( $\chi$ = 1.2-1.35)	0.25 to 0.4	33
Pulsed/Damped ratio	2.2 to 3.9	2.5 to 4.5	2.6

Understanding the origin of the enhanced mass transfer in pressure-pulsed flow, we can predict the conditions to further increase the limiting currents. We believe that  $CO_2R$  current densities of >100 mA cm<sup>-2</sup> can be achieved if higher f,  $P_{PP}$  and/or  $\chi$  were applied in our system. At the same time, increasing f,  $P_{PP}$  and/or  $\chi$  alone would also require new equipment and additional pumping energy. Considering the effectiveness of combining high  $CO_2$  concentrations with enhanced mass transport (as shown in Figure 5.4D with the exsolution strategy), we highlight the potential of using elevated pressure together with high  $P_{PP}$ . An elevated pressure increases the  $CO_2$  concentration, while a higher  $P_{PP}$  enhances the mass transfer. While  $\chi$  is compromised by elevated pressure, the  $P_{PP}$  is not, thereby allowing high  $CO_2$  concentrations and simultaneous fast mass transfer for obtaining even higher limiting current densities that could compete with gas-fed  $CO_2$  electrolyzers.

# **5.2.4.** Outlook for the implementation of pressure pulsed flow for $CO_2R$

To assess the potential for scaling and implementation of this technology, we consider three potential issues 1) Energy consumption of the pump, 2) contaminations and temperature effects due to the pump, and 3) damping of the pressure waves by gas bubbles upon scaling.

The compression of the electrolyzer during the pressure pulsed flow requires energy. A calculation of the energy requirements, based on the thermodynamic work, is performed in 5.5.12. The FE-VE of the pulsed system in Figure 5.4D would decrease from 30-40% to 22-28%, when this compression energy is included. This decrease is more pronounced at lower current densities. However, the actual energy consumption of the pump (based on a power meter) is much higher than this calculation, as coffee pumps are not designed for energy efficiency. At the same time, the flow rate of this pump is highly oversized for the electrode area (2 cm<sup>2</sup>). Based on the solubility of CO<sub>2</sub> (33 mM at 25 °C) and a partial CO-eq. current density of 87 mA cm<sup>-2</sup>, we calculate that this flow rate provides more than 150x the required CO<sub>2</sub>. Hence, a lower flow rate (e.g. by creating the pressure oscillations with a additional piston instead of at the pump itself[40]) would be a potential lever to decrease the energy consumption while maintaining high production rates.

Because the vibratory pump produces a significant amount of heat, the electrolyte temperature increased by 8 to 10 °C over the course of the experiment. This higher temperature increases the ohmic resistance of the coil, which results in a lower  $P_{\rm PP}$  and  $\chi$  (see 5.5.13) and reduces the CO<sub>2</sub> solubility, causing a 10-30% lower  $j_{\rm CO-eq}$  after 35 minutes (see 5.5.11).

Alternatively, the decrease in  $FE_{CO}$  over time (see 5.5.14) can also be caused by contamination. We detected iron contamination at the electrode (20 to 40 ppm versus 5 ppm on electrodes with a stable  $FE_{CO}$ , see 5.5.14), possibly polluted from the pump interior or impurities in the KHCO<sub>3</sub>. This high sensitivity of the  $FE_{CO}$  to ppm levels of iron has also been observed by others[7, 8]. The electrodes do not seem to be damaged by the pressure pulses, as the silver microstructures seem unchanged after 40 min of pulsation (see SEM images in 5.5.15).

Finally, we considered the damping of pressure pulses during CO<sub>2</sub>R experiments (Figure 5.5A), which is important for scaling up. Figure 5.5B shows pressure waves at 30 and 200 mA cm<sup>-2</sup> at the inlet and outlet of the electrolyzer. We observed a reduction of  $P_{\rm PP}$  and  $\chi$  at the outlet, which was more pronounced at higher current densities. We define damping with Eq 5.6:

$$Damping(\%) = \frac{\chi_{Inlet} - \chi_{Outlet}}{\chi_{Inlet} - 1}$$
(5.6)

Here  $\chi_{\text{Inlet}}$  and  $\chi_{\text{Outlet}}$  are the relative expansion at the inlet and outlet of the electrolyzer. The system fully damps the pressure pulses if  $\chi_{\text{Outlet}}$  is 1. Figure 5.5C shows the effect of current density on damping. A steep increase in damping can be observed up to 90 mA cm<sup>-2</sup> after which the increase is more gradual. Because the damping increases with the current densities, we hypothesise that electrolytic gas bubbles inside the electrolyzer are the main cause of the damping. We expect the damping to increase for larger



Figure 5.5: A. Graphical representation of pressure wave damping through a  $CO_2R$  electrolyzer B. Pressure waves at the inlet and outlet of the electrolyzer at 30 and 200 mA cm<sup>-2</sup> C. Time averaged damping (Eq 6) versus current density. Damping is calculated over 40 min, where the first 5 min are skipped to ensure a steady gas bubble state is achieved. The error bars indicate the standard deviation calculated over duplicate measurements.

electrolyzers as there will be more gas bubbles in the system. The damping at the anode is stronger than at the cathode because of  $CO_2$  bubbles are formed by recombination of  $H^+$  and  $HCO_3^-$ , which makes the ratio of electrons to gas molecules at the anode and cathode 1.25 and 0.5, respectively. Unfortunately, damping reduces the effectiveness of the pressure pulses and therefore also reduces the mass transport. Thinner flow compartments with good bubble removal, which reduce the total gas bubble volume, could mitigate this effect.

# **5.3.** CONCLUSION

This work introduced a pressure pulsed aqueous  $CO_2R$  electrolyzer. Using a cheap vibratory pump (~18 euro), typically found in coffee machines, fast pressure pulses (50 Hz, 1-2.5 bar) were generated to improve the mass transport of dissolved  $CO_2$  to the cathode. High current densities for  $CO_2R$ , up to 87 mA cm<sup>-2</sup>, are obtained using a commercial silver mesh cathode, outperforming all H-cells in literature and even most aqueous systems with elevated pressure. The limiting current density towards  $CO_2R$  products was 2.6 times higher compared to a system where the pressure waves were damped. Through a high-speed imaging analysis, PIV and order of magnitude scaling, we identified that the enhanced mass transport is caused by oscillating gas bubbles and a multidirectional oscillatory flow.

Three potential engineering challenges were identified that could limit the implementation and scaling of this technology: 1) high energy consumption of the pump, 2) contaminations and temperature effects due to the pump, and 3) damping of the pressure waves by gas bubbles upon scaling.

On the other hand, the pressure-pulsed flow could be further leveraged by increasing the pressure wave frequency (f), peak-to-peak pressure ( $P_{PP}$ ) and relative expansion ( $\chi$ ). Combining this optimization of the pumping parameters with using a more selective electrode and applying higher CO<sub>2</sub> concentrations (e.g. through supersaturated electrolytes), even higher limiting current densities could be achieved. Altogether, the pressure-pulsed concept could make aqueous CO<sub>2</sub>R a viable alternative to state-of-theart gas-fed electrolyzers.

# **5.4. EXPERIMENTAL PROCEDURES**

# 5.4.1. PRESSURE PULSED CO<sub>2</sub> REDUCTION SETUP

The pressure pulsed  $CO_2R$  setup consisted of a vibratory pump, an electrolyzer, a back pressure regulator and an electrolyte container with connections to a  $CO_2$  gas bottle and gas chromatograph (GC), see Figure 5.6A (for photos of the setup, see 5.5.16). The vibratory pump (Ulka EP5) was controlled with a variable frequency drive (VFD, Schneider Electric ATV12H037M2). This VFD model requires three phases as output, therefore we installed two other vibratory pumps that were circulating water in a separate reservoir. All three pumps were placed in a grounded aluminium box. During damped pressure pulse experiments, we installed two pressure dampers (FPD 1.10 KPZ, KNF) between the pump and the electrolyzer inlet.

The electrolyzer consisted of two 3D printed acrylate (PMMA) backplates, and two laser cut transparent 4 mm thick PMMA flow channels (Figure 5.6B, drawings in 5.5.16). A commercial silver mesh (80 woven, 0.115 mm diameter wire, 99.9% Thermo Scientific) was used as the cathode and a titanium plate coated with mixed metal oxide (Ir/Ru, PSC-101 Permascand) was used as the anode. The two channels were separated with a Zirfon PERL UTP 500 separator, which was used for its good conductivity and mechanical strength. To minimize pressure differences across the diaphragm, only one pump was used for both the anode and cathode compartment. Catholyte and anolyte were collected and mixed in the same electrolyte bottle. Silicone gaskets (0.5 mm thickness) were used for sealing. Both the cathode and the anode have an exposed geometric electrode area of 2 cm<sup>2</sup> and were electrically connected to the potentiostat with Ag wires (0.25 mm diameter, 99.99%, Agosi AG). The electrolyzer was operated in a 4-electrode configuration. A LF-1-45 leak-free Ag/AgCl (Innovative Instruments) was used as the reference electrode and an additional Ag wire connected to the cathode as the sense electrode. The cell was designed to handle pressures up to 7 bar.

The amplitude of the pressure pulses was controlled with a back pressure regulator (Swagelok SS-1R4F) at the outlet of the cell. The pressure was recorded by four pressure transmitters (PT, TC-Direct 716-908), which were connected to T-junctions at the inlets and outlets of the electrolyzer. The temperature was measured by pressing thermocouples (K-type, TC Direct-405-011) against the tubing (see Figure 5.6A). The pressure transmitters and thermocouples were read out with NI-9205 and NI-9213 modules at 5000 and 1 Hz respectively.

#### **5.4.2.** EXPERIMENTAL DESCRIPTION

For each experiment, 200 mL of fresh liquid electrolyte ( $0.5 \text{ M KHCO}_3$ , 99.5+% Thermo Scientific) was continuously bubbled with 100 mL min<sup>-1</sup> of CO<sub>2</sub>. The gas headspace in the electrolyte container was 100 mL. The experiments were performed over ~40 minutes under constant current, controlled by an Ivium XP20 potentiostat. A GC sample was taken from the electrolyte container headspace every 3.5 min (Compact GC4.0, Interscience). The methods and setup of Baumgartner et. al.[17] were used to calculate the faradaic efficiency of gas products. A liquid sample was taken at the end of the ex-

periment and analysed with HPLC (1290 Infinity II, Agilent) according to the methods of Kortlever et. al.[32]. The faradaic efficiency of liquid products was assumed constant over an experiment, due to lack of time-resolved data. The starting temperature of the electrolyte was between 18 and 22 °C. The pump generated a significant amount of heat, which caused the temperature to increase by 8 to 10 °C over the 40 minutes. The electrolyte container was placed in an ice bucket to limit the temperature to 35 °C.



Figure 5.6: A. Diagram of the pressure pulsed CO2 reduction setup, TC: Thermocouple, PT: Pressure transmitter, PR: Back-pressure Regulator, GC: Gas Chromatograph B. Graphical representation of the CO<sub>2</sub> electrolyzer. See 5.5.16 for a photo and a more detailed diagram of the electrolyzer.

# **5.4.3.** Electrode pre-treatment

Before each experiment, a fresh cathode was cleaned by holding it in a propane flame. The cathode was then placed inside the cell and anodized for 1 min by applying a current density of 10 mA cm<sup>-2</sup>. After flushing the cell with fresh electrolyte, the experiment was started, leading to a reduction of the oxidized silver surface and resulting in a roughening of the silver surface (5.5.17). The pre-treatment of the cathode with a constant anodizing current almost doubled the faradaic efficiency towards CO and increased the catalyst stability over time (5.5.17).

# 5.4.4. HIGH-SPEED IMAGING

High-speed imaging and PIV were used to investigate the mixing phenomena and velocity fields inside the electrolyzer. To make the channel more transparent, a glass microscope slide was glued to the outside of the channel with Araldite 2020. A LaVision Imager HS 4M camera was used for imaging at a rate of 3.7 kHz. The electrolyte used during the PIV measurements was demineralized water seeded with 4  $\mu$ m tracer particles (PS-FluoRed-Fi191, GmbH). For a detailed description of the imaging setup and method see 5.5.7.

# **5.5. SUPPLEMENTARY INFORMATION**

#### 5.5.1. ENERGY REQUIREMENT FOR CO<sub>2</sub> EXTRACTION

A gas-fed CO<sub>2</sub>R electrolyzer requires a relatively pure CO<sub>2</sub> inflow stream. When CO<sub>2</sub> is captured from an environmental source, like in direct air or direct ocean capture, the CO<sub>2</sub> first needs to be extracted from the capture liquid. Sabatino et. al.[21] show in their work that the energy to extract, purify, concentrate and pressurize the CO<sub>2</sub> from the capture solutions is in the order of 1-5 MJ kg<sup>-1</sup> CO<sub>2</sub> for different capture technologies (direct air capture with alkaline, amine or solid sorbents).

To indicate the magnitude of this energy requirement, we will compare it to the energy consumption of a CO<sub>2</sub> electrolyzer, which operates at a cell voltage ( $E_{Cell}$ ) of 3 V and a faradaic efficiency (FE<sub>CO</sub>) of 100%. Below the energy consumption for converting 1 kg of CO<sub>2</sub> to CO is calculated.

- $1 \text{ kg CO}_2 / 44.01 \text{ g mol}^{-1} \text{ CO}_2 = 22.72 \text{ mol CO}_2$
- 22.72 mol CO<sub>2</sub> · 2  $e^{-}$ /CO<sub>2</sub> · 96485 C mol<sup>-1</sup>  $e^{-}$  = 4.38·10<sup>6</sup> C kg<sup>-1</sup> CO<sub>2</sub>
- $4.38 \cdot 10^6 \text{ C kg}^{-1} \text{ CO}_2 \cdot 3 \text{ V} \cdot 100\% = 1.32 \cdot 10^7 \text{ J kg}^{-1} \text{ CO}_2 = 13.2 \text{ MJ kg}^{-1} \text{ CO}_2$

The CO<sub>2</sub> extraction costs are therefore  $\sim$  10-35% of the energy consumption of a gas-fed CO<sub>2</sub> electrolyzer.

#### **5.5.2.** EXTRA PEAKS IN THE PRESSURE WAVE

To investigate the cause of extra peaks in the pressure pulses, we tested the pump after removing most components of the CO<sub>2</sub>R setup (Figure S5.1). A setup with only 15 cm of tubing after the vibratory pump resulted in a cleaner pressure wave, better resembling a half-rectified sine wave. We therefore assume the secondary waves in the pressure pulses originate from vibrations and reflections in the electrolyzer, tubing and pressure reducing valve and not from the pump. The peak pressure ( $P_{\text{peak}}$ ) is also reduced, which can mainly be attributed to the removal of the pressure regulator after the electrolyzer.



Figure S5.1: Investigation of extra peaks in the pressure pulses. A. Pressure pulses of demineralized water inside the normal CO<sub>2</sub>R setup and B. if only 15 cm of tubing was installed after the pump.

#### **5.5.3.** EFFECT OF DAMPERS ON THE FLOWRATE

To measure the effect of the pressure dampers on the pump flowrate, demineralized water was pumped for 30 s into a bottle. The bottled was weighed and the flowrate was calculated by repeating this and taking the average (see Figure S5.2). 998.2 g L<sup>-1</sup> was used as density of water (20 °C, atm). The normal flowrate over six measurements was  $533 \pm 14 \text{ mL min}^{-1}$ , and with dampers  $530 \pm 14 \text{ mL min}^{-1}$ . The flowrate difference is less than 1%, and is smaller than the error. The pressure dampers therefore have no significant effect on the flowrate. We assume the flow is equally split between the anode and cathode compartments, which would be a flowrate of 266 mL min<sup>-1</sup>. The cross-sectional area of the compartment is 1.0.5 cm = 0.5 cm<sup>2</sup>. The average velocity is therefore ~8.9 cm s<sup>-1</sup>.



Figure S5.2: A. Setup for flowrate determination of the Ulka EP-5 vibratory pump, with and without dampers. B. Boxplots of the mass of the liquid after pumping for 30 seconds.

# 5.5.4. AVERAGE PRESSURE, RELATIVE EXPANSION AND PRESSURE DROP DUR-ING CO<sub>2</sub>R EXPERIMENTS

Figure S5.3 below show the time averaged pressure ( $P_{avg}$ ) at different current densities during the CO<sub>2</sub> electrolysis experiments at the inlet of the electrolyzer. The pressure for all damped pressure pulses is up to 100 mbar lower. We attribute this to the additional pressure drop over the pulsed dampers.



Figure S5.3: A. Time averaged pressure ( $P_{avg}$ ) during the pressure pulsed CO<sub>2</sub> reduction experiments. B. Relative expansion ( $\chi$ ) the pressure pulsed CO<sub>2</sub> reduction experiments. The error bars are the standard error over duplicate measurements.



Figure S5.4: Time averaged pressure drop at various current densities, for pressure pulsed (Puls), damped (Damp) at the anode (A) and cathode (C). This value is the difference between the pressure measured at the inlet and outlet PT, which are 40 cm apart.

# 5.5.5. CATHODE VOLTAGE OF PRESSURE PULSED CO<sub>2</sub>R EXPERIMENTS

The cathode voltage of the pressure pulsed  $CO_2$  reduction experiments was measured against a Leak-free Ag/AgCl micro reference electrode, positioned close to the electrode. The error bars of the cathode voltage are relatively large, which we attribute to gas bubbles sometimes blocking the active area of the reference electrode, causing large spikes in the voltage, and causing differences between duplicate measurements.



Figure S5.5: A. Cathode voltage vs CO partial current density. B. Cathode voltage vs total current density, averaged over duplicates. All error bars are the std error over 2 duplicate measurements (except for 70 mA cm<sup>-2</sup> in the damped flow, which was a single measurement).

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Table S5.1: Literature comparison of CO<sub>2</sub>R performance of aqueous CO<sub>2</sub> reduction systems, data is plotted in Figure 5.3D. These works were selected as they reported current densities up to limiting current densities.

s/Yéar	Type Direct Bicork	Electrode Cu	<i>j</i> CO-eq (mA cm <sup>-2</sup> ) 49.7	FE (%) 33	E <sub>Cath</sub> (V vs RHE)	Ecell (V) 4.27	FE-VE (%) <sup>A</sup> 10	Notes Based on j <sub>HCOO</sub> – from Figure 3C @400 mA cm <sup>-2</sup>
110)22()	DIFECT BICATD.	Cu/Co(O)CNT	50.8	43	c	4.48	13	Based on $j_{HCOO}$ from Figure 3C @350 mA cm <sup>-2</sup>
114[44]	Tao-tr	gy	1.0	10	C.1-		G	from Figure 6 and converted with F-2 (2e <sup>-</sup> :CO)
12[45]	H-Cell	Au <sub>25</sub> clusters	16.1	66	-1.0		51	Used CO current from Figure $3a/b$ (assumed 99% FE to CO, as H <sub>2</sub> formation is $10^2$ smaller)
46]	H-Cell	Ag Nano Part.	18.6	93	-0.6		56	Assumed 93% FE <sub>CO</sub> and 20 mA cm <sup><math>-2</math></sup> $j_{tot}$ from Fig- ure 2 smaller)
16[47]	H-Cell	Ag(Ox)	2.9	95	-0.9		51	Assumed 95% FE <sub>CO</sub> from Figure 3 and 3% FE <sub>HCOO</sub> from SI
on 2017[6]	Bubble Induc.	Au Nanoneedle	58.0	95	-0.5		60	Assumed a FE of 95% from Figure 5, overpotential of 0.4 V, CO starts at -0.1 V vs RHE
	H-cell		26	13	-3.3		4	1 bar measurements (Figure 2E)
ntecave 2020[48]	Elev. Pres.	Ag on Zn	134	67	-2.0		25	3 bar measurements (Figure 2E)
	Elev. Pres.	117 110 917	188	94	-1.2		45	6 bar measurements (Figure 2E)
	Elev. Pres.		296	74	-2.3		25	9.5 bar measurements (Figure 2E)
	H-Cell		1.2	53	-1.12		26	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [1]
	H-Cell		7.8	67	-1.30		31	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [2]
	H-Cell		9.7	73	-1.22		34	Maximum <i>j</i> <sub>CO-eq</sub> <sup>6</sup> from Table S1 – Exp [3]
	Elev. Pres.		3.5	56	-1.25		26	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [4]
	Elev. Pres.		14.3	73	-1.59		30	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [5]
	Elev. Pres.		19.3	77	-1.51		33	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [6]
[28]	Elev. Pres.	Cu plate	8.0	64	-1.42		28	Maximum <i>j</i> <sub>CO-eq</sub> <sup>2</sup> from Table S1 – Exp [7]
	Elev. Pres.		26.4	69	-2.04		25	Maximum <i>j</i> <sub>CO-eq</sub> <sup>6</sup> from Table S1 – Exp [8]
	Elev. Pres.		32.0	75	-2.00		28	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [9]
	H-Cell		5.4	29	-1.80		11	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [10]
	Elev. Pres.		23.0	51	-2.54		16	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [11]
	H-Cell		8.8	69	-1.18		33	Maximum <i>j</i> <sub>CO-ed</sub> from Table S1 – Exp [12]
	Elev. Pres.		21.6	50	-1.62		20	Maximum <i>j</i> <sub>CO-eq</sub> from Table S1 – Exp [13]

Authors/Year	Type	Electrode	JCO-eq	FE	ECath	$E_{Cell}$	FE·VE	Notes
			$(mA cm^{-2})$	(%)	(V vs RHE)	(V)	$(\%)^{A}$	
		Cu-(B)-2	18.4	62	-1.1		39	
Zhou Sargent 2018[50]	H-Cell	Cu-(H)	14.6	56	-1.1		28	
		Cu-(C)	20.0	67	-1.1		33	
Clark 2018[49]	H-Cell	Polycrys. Ag	9.4	87	-1.35		39	H-Cell (Figure 3B/3D)
			45.6	73		4.25	23	Data taken from Table S1
Obasanjo Dinh 2023[8]	Direct Bicarb.	Cu-Mesh	92.9	74		5.4	18	Data taken from Table S1
			127.1	68		7.57	12	Data taken from Table S1
			1287	92		4.5	27	Exsolution cell (1 cm <sup>2</sup> ) (Figure 5C)
Wen Chen 2022[38]	Exsolution	Ag on Carb. felt	1054	87		3.7	31	Exsolution cell $(4 \text{ cm}^2)$ (Figure 5D)
			802	88		4	29	Exsolution cell $(100 \text{ cm}^2)$ (Figure 5E)
Oi Voiry 2023[29]	Fley Pres	CiletAge	7.1	40	-0.73		23	H-Cell (supplementary table 8) (assumed 10 bar for
		09, 78,00						supersaturation, product composition from figure
			010					JUJ ITick mussimus alastushiran (simulamontami Takla 0
			0.4.0	10	-0.1		сс С	rugn pressure electroryzer (supplementary table o,
								assumed same ratio of other compounds as H-cell
			010	01	01.0		4	experiment)
			21.0	77	-0./8		40	
			35.9	72	-0.95		38	
This work	Dulead	Ag mach	6.99	74	-1.31		34	
TILLS WULK	n nocin I	TIGOTTI SU	76.8	59	-1.68		24	
			87.6	56	-1.56		24	
			73.9	39	-1.84		15	
			22.0	73	-0.81		40	
			32.7	99	-1.07		33	
			33.0	50	-1.15		24	
This work	Damped	Ag mesh	21.7	26	-1.26		12	
	I	1	24.7	19	-1.19		6	
			20.5	13	-1.76		5	
			20.2	11	-1.74		4	
A: The VE was calculated with	h two methods,	depending on w	hat was repor	ted in	the articles. I	If cell pc	otential (	$E_{Cell}$ ) was reported, the VE was calculated as VE =
$E_0/E_{Cell}$ , where $E_0$ is the stant where we assume a anode pot	dard cell potenti ential for the OF	al for the reaction 3R of 1.6 V vs RHE	1 2CU2 -> 2CU	0+02,	which is 1.33	V[54]. II	the cath	ode potential was reported, $VE = E_0/(1.6 \text{ V} - E_{\text{cath}})$ ,

# **5.5.7. HIGH-SPEED IMAGING AND PARTICLE IMAGE VELOCIMETRY (PIV)** The pressure pulsed CO<sub>2</sub>R setup was slightly modified for high-speed imaging (Figure S5.6):

- The potentiostat was disconnected, and the electrolyte was replaced with demineralized water seeded with 4 µm diameter fluorescent tracer particles (PS-FluoRed-Fi191, GmbH). Deen et. al. have discussed that PIV on gas-liquid flows with gas fractions of >2% will result in large measurement inaccuracies[55]. We therefore chose to use demineralized water instead of saturated electrolyte, since the small amount of bubbles will result in more accurate velocity fields. Some gas bubbles were still present in the electrode and electrolyte due to cavitation in the pump and small ambient temperature changes during the day.
- A glass microscope slide was glued to the outside of the flow channel to improve the transparency with Araldite 2020 two component epoxy glue.
- An Imager pro HS 4M high-speed camera (LaVision) was installed on the side, parallel to the cathode to look inside the channel. A Navitar lens with 0.58-7 magnification was mounted on the camera and set to 1.5x or 3x during the measurements. The imaging framerate during PIV experiments was 3.7 kHz. The camera was installed at a slight (2-3°) angle to make sure the electrode was visible (at 0°, the gaskets would block the view).
- For the high-speed videos, the cell was illuminated from the back with a desk lamp.
- For the PIV measurements, the cell was illuminated from the bottom by a double pulsed Nd:YLF laser (IDY304, Litron Lasers, England). A beam focuser (VZ-Sheet, thin, 532 nm, collimated, ITM000969802) was used to focus the laser into a thin sheet to only illuminate the tracer particles in a thin layer of fluid in the electrolyzer and a 540 nm long-pass filter was installed in front of the camera to make sure only the fluorescence is measured, and not the reflections of the 527 nm laser light.



Figure S5.6: A. Schematic of the high-speed imaging setup, green arrows represent laser light, red arrows fluorescence from the PIV particles B. Photograph of the imaging setup

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**PIV processing** The length in the PIV images were calibrated using the distance between two strands of the Ag mesh cathode, which was visible inside the flow channel. The distance between the centre of two adjacent threads of the mesh is  $292 \,\mu$ m. The images were pre-processed with two steps: First, a geometric mask is applied over the flow channel remove reflections of the electrode and particles stuck on the electrode from the image. Next, a subtract sliding minimum time filter was subtracted to minimize background noise.

After pre-processing, the images were converted into a velocity field with the PIV module of the DaVis software. The PIV was performed with two steps: the initial displacement vector was calculated with an interrogation window of 256 x 256 pixels, with 50% overlap. The second step of the PIV was performed with a smaller interrogation window was 64 x 64 pixels. An overlap of 75% was used with four passes.

**Processing of the velocity fields** The velocity fields of the pulsed and the damped pressure waves case were compared by taking a spatial average. The  $v_x$  (velocity in the direction of the cathode) and  $v_y$  (velocity in the flow direction, parallel to the cathode) were averaged at three vertical lines parallel to the cathode at distances of 0.05, 0.10 and 0.25 mm from the cathode. Since the velocity between pressure waves differed slightly, the velocity profiles were averaged over ten pulses, see Figure S5.7.



Figure S5.7: Postprocessing of PIV data to generate the velocity plots used in Figure 5.4 in the paper. (Left) Example of a PIV velocity field. The color bar indicates the magnitude of the velocity in the x direction (towards the right).

# 5.5.8. Y-VELOCITY FROM PIV AND OUTLET PRESSURE GRADIENT



Figure S5.8: A. Average fluid velocity parallel to the electrode ( $v_y$ ), averaged over 10 pulses. The time on the horizontal axis corresponds to that in Figure 5.4B B. Comparison of the pressure gradient measured at the outlet of the electrolyzer(d $P_{\text{Outlet}}/dt$ ) to  $v_x$  at the electrode

### 5.5.9. PIV RESULTS OF THE DAMPED PRESSURE WAVES

Below are the PIV results of the damped pressure pulsed flow regime. For the conditions, please refer to 5.5.7.



Figure S5.9: PIV results of the damped pressure pulsed flow. A. Pressure versus time profile (we acknowledge that this wave is more significantly damped than other experiments, and do not have a good explanation for this). B. Average velocity perpendicular to the electrode ( $v_x$ ) and C. Parallel to the electrode ( $v_y$ ) at three distances from the electrode. All velocities are averaged over 10 pressure pulses.

# 5.5.10. Order of magnitude comparison of the pressure gradients

To understand the significance of the pressure wave compared to the pressure drop over the electrolyzer, we will perform an order of magnitude comparison. The pressure drop, dP/dy was measured, and is show in Figure S5.4. It is between 0 and 50 mbar. To be conservative we will used 50 mbar in the order of magnitude comparison. The distance between the inlet and outlet pressure sensors is 40 cm, however, we will assume that all the pressure drop happens inside the electrolyzer, which has a length of ~6 cm, including connections to the tubing. This results in a pressure drop over the cell of  $8.3 \cdot 10^4$  Pa m<sup>-1</sup>. The pressure drop due to oscillations is calculated with the following equation:

$$\left(\frac{\mathrm{d}P}{\mathrm{d}y}\right)_{\mathrm{osc}} = \frac{1}{c_{\mathrm{wave}}} \frac{\mathrm{d}P}{\mathrm{d}t} = \frac{1}{c_{\mathrm{wave}}} \frac{P_{\mathrm{PP}}}{0.1/f}$$
(S5.1)

Here,  $c_{\text{wave}}$  is the speed of the pressure wave inside the electrolyzer,  $P_{\text{PP}}$  is the peak to peak pressure and f the frequency.  $c_{\text{wave}}$  is calculated as follows:

$$c_{\text{wave}} = \frac{\mathrm{d}y}{\mathrm{d}t} \tag{S5.2}$$

Where dy is the distance between the two pressure transmitters and dt the time it takes for a pressure wave to travel there. Figure 5.5B shows that dt is 7 ms, the distance between the two pressure sensors (dy) is 40 cm, resulting in a  $c_{wave}$  of 57 m s<sup>-1</sup>, which is a realistic speed in for a gas-liquid flow[56].

The pressure gradient during a pressure pulse then becomes:  $1.1 \cdot 10^6 \text{ Pa m}^{-1}$ .

As the pressure gradient from pressure pulses is an order of magnitude larger than the pressure drop over the cell, we conclude that it is significant for the mass transport.

# **5.5.11.** DECREASE OF $j_{CO-eq}$ OVER TIME AND CORRELATION ANALYSIS



Figure S5.10: *j*<sub>CO-eq</sub> at various total applied current densities, after 6 and 40 min of experiments, all current densities were investigated two times.

Figure S5.10 shows that the  $j_{\text{CO-eq}}$  reduces by 5 to 30% after 40 minutes of measurements. This is a result of the mass transport limitations at the end of an experiment, as the decrease in  $j_{\text{CO-eq}}$  is larger at higher current densities. We believe this worse mass transport is mainly caused by the lower  $P_{\text{PP}}$  and  $\chi$  (see Figure S5.13), which are caused by the heating up of the vibratory pump.

To further investigate this, we performed a statistical analysis (Pearson correlation coefficient) on the  $P_{PP}$  and  $j_{CO-eq}$  versus time datasets (Figure S5.11). The  $P_{PP}$  and  $j_{CO-eq}$  are strongly correlated at high applied current densities, indicated by a correlation value of close to 1. This can be interpreted as: "When the  $P_{PP}$  is lower, the resulting  $j_{CO-eq}$  will be lower to." This effect is more pronounced at higher applied current densities, where mass transport limitations are more pronounced. Here the results of a decrease in  $P_{PP}$  is more visible in the resulting  $j_{CO-eq}$ . As it takes some time for the samples to travel to the GC, we also investigated the correlation coefficient with a lag time of 1 GC sample (206 s).



Figure S5.11: Correlation coefficients between the  $j_{\text{CO-eq}}$  and  $P_{\text{PP}}$  at various applied current densities. A. Lag time of 0 s. B. Lag time of 206 s, the time between two GC samples.

# 5.5.12. CALCULATION OF THE ENERGY COSTS REQUIRED FOR PRESSURE PULSES

The following assumptions were made to calculate the energy requirements for pressure pulsed flow:

- Gas fraction (*x*<sub>gas</sub>) of 2%
  - Liquid flowrate: 266 mL min<sup>-1</sup> in catholyte flow channel 266 mL min<sup>-1</sup> / 60 s min<sup>-1</sup> / 1000 = 4.4  $10^{-3}$  L s<sup>-1</sup>
  - Gas production rate: 400 mA (worst case assumption) 0.4 A / 96485 C mol<sup>-1</sup> / 2 e<sup>-</sup>/gas  $\cdot$  24.0 L mol<sup>-1</sup> = 5.0 10<sup>-5</sup> L s<sup>-1</sup>
  - Gas/total = 1.1%, we will use 2% a conservative approach
- · Liquid is incompressible, all compression costs are gas compression
- Adiabatic process
- Ideal gas

The compression cost during the pressure pulse are defined as follows:

$$dW = P_{\text{peak}}dV \tag{S5.3}$$

Where dW is the performed work in J,  $P_{\text{peak}}$  is the peak pressure of a pulse in in Pa, and dV is the change in gas volume during the pressure pulse in m<sup>3</sup>, which is calculated as follows:

$$dV = V_{\text{cell}} x_{\text{gas}} \left( \frac{1\text{bar}}{P_{\text{peak}}} - 1\text{bar} \right)$$
(S5.4)
Where  $V_{\text{cell}}$  is the volume of the electrolyzer and tubing until the back pressure valve (in m<sup>3</sup>),  $x_{\text{gas}}$  is the gas fraction (2%) and  $P_{\text{peak}}$  is the peak pressure in bar. For these experiments  $V_{\text{cell}}$  is 2 cm<sup>2</sup>  $\cdot$  0.5 cm = 1 mL, or 1 10<sup>-6</sup> m<sup>3</sup>. The power required for a pulsed flow is then defined as follows:

$$Power_{\text{pulses}} = \mathrm{d}W \cdot f \tag{S5.5}$$

Where  $Power_{pulses}$  is the required power in W and f is the frequency of the pressure pulses in Hz.  $Power_{pulses}$  is then converted into an equivalent voltage ( $U_{pulses}$ ) as follows:

$$U_{\text{pulses}} = \frac{Power_{\text{pulses}}}{I} = \frac{Power_{\text{pulses}}}{j \cdot A}$$
(S5.6)

Where *I* is the current in A, *j* is the current density in A cm<sup>-2</sup> and *A* is the electrode area in cm<sup>2</sup> which was 2 cm<sup>2</sup> for the pressure pulsed CO<sub>2</sub> electrolyzer. The energy requirement for various current densities is shown below in Figure S5.12, and included into the literature comparison from Figure 5.3D.



Figure S5.12: A. Equivalent voltage costs of of the pressure pulses versus current density B. Literature comparison from Figure 5.3D when pump energy costs are included

#### **5.5.13.** $P_{PP}$ and $\chi$ over time



Figure S5.13: A. Peak to peak pressure ( $P_{PP}$ ) and B. relative expansion ( $\chi$ ) over the time of a CO<sub>2</sub>R experiment for different current densities. The error bar is the standard deviation over 10< seconds (500+ pressure pulses) during the recording.

**5.5.14.** DISCREPANCY IN THE FE BETWEEN DUPLICATE MEASUREMENTS

Figure S5.14 shows three outliers in the pressure pulsed  $CO_2$  experiments that performed significantly worse compared to their duplicate experiment. We attribute this worse performance to metal contaminations. We believe some of the iron impurities came from newly installed vibratory pumps, impurities in the KHCO<sub>3</sub> batch and possibly dirty glassware.



Figure S5.14: Faradaic efficiency over time for pressure pulsed  $CO_2R$  experiments at A. 30 mA cm<sup>-2</sup> B. 50 mA cm<sup>-2</sup> C. 200 mA cm<sup>-2</sup>. The right column contains outliers in the duplicate experiments, which have much worse FE trends. This is attributed to metal contaminations on the cathode.

Table S5.2: Contaminations on electrodes as measured with ICP. The electrode samples are the same as the  $CO_2R$  experiments in Figure S5.14

ICP Sample	Ag [m%]	Cu [ppm]	Fe [ppm]	Zn [ppm]
50 mA cm <sup>2</sup> (good)	100.6	65.9	4.9	3.1
50 mA cm <sup>2</sup> (poor)	99.6	42.0	40.0	4.6
30 mA cm <sup>2</sup> (poor)	99.6	58.2	18.5	3.9

#### **5.5.15.** EFFECT OF PRESSURE PULSES AND CURRENT DENSITY ON THE ELEC-TRODE MICROSTRUCTURES



Figure S5.15: SEM images of electrodes after 40 minutes of electrolysis experiments. No significant differences in the microstructures were observed. x10000 magnification, the scalebar is 1  $\mu$ m

#### 5.5.16. PHOTOS OF SETUP AND DRAWING OF ELECTROLYZER



Figure S5.16: Drawings of the electrolyzer



Figure S5.17: Photograph of the setup. The pumps are inside a box, placed on a foam to reduce vibration.

#### 5.5.17. Effect of pretreatment on CO<sub>2</sub>R performance

Pre-treated cathodes resulted into much more stable and better performing CO<sub>2</sub>R (Figure S5.18). All cathodes were pretreated by applying an anodic current of 10 mA cm<sup>-2</sup> before the experiment. This removed dissolved from the silver, and creates a small layer of Ag<sub>2</sub>O. Once the experiment start the Ag<sub>2</sub>O is reduced back into silver microstructures (Figure S5.19). The performance increase is similar to what was observed by Ma et. al.[46].



Figure S5.18: Faradaic efficiency over time for a pre-treated (A) and untreated (B) cathode. Operating conditions.  $0.5 \text{ M KHCO}_3$ , 50 mA cm<sup>-2</sup>, pressure pulsed electrolysis.



Figure S5.19: Scanning electron microscope (SEM) images of a pre-treated silver mesh cathode (Left) and untreated electrode (Right) at 10000x magnification, scale bar is 1  $\mu$ m. SEM model: JSM-IT700HR

### **5.6.** SUPPLEMENTARY VIDEOS



Video S5.20: 100x slow-motion video during pressure pulsed CO<sub>2</sub>R at 50 mA cm<sup>-2</sup>. https://www.youtube.com/watch/ogQLQ0A3MIQ



Video S5.21: 100x slow-motion video during pressure pulsed CO<sub>2</sub>R at 130 mA cm $^{-2}$ . https://www.youtube.com/watch/ZoZqwbxrWi8



Video S5.22: 100x slow-motion video during damped CO\_2R at 50 mA cm $^{-2}$ . https://www.youtube.com/watch/QYqCOi-C7WY



Video S5.23: 100x slow-motion video during damped CO\_2R at 130 mA cm $^{-2}$ . https://www.youtube.com/watch/6uMuX8VE6YQ



Video S5.24: Slow-motion video during a PIV measurement, where bubbles move into the Ag mesh cathode. https://www.youtube.com/watch/rnmALR0VxCA



Video S5.25: Real time video during pressure pulsed CO<sub>2</sub>R at 160 mA cm<sup>-2</sup>. https://www.youtube.com/watch/ORFdmQ5JXmY

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# 6

## **REFLECTION AND OUTLOOK**

This thesis started by highlighting the significance of gas evolving electrolysis processes for the energy transition. These processes are currently still too expensive to compete at a large scale with their fossil-fuel based counterparts. Gas bubbles could play a crucial role in the development of more efficient electrolysers; in Chapter 2, I show that gas bubbles compromise the electrolyser performance by increasing the resistance, whereas in Chapter 4 and 5, I show that gas bubbles can also benefit electrolysers as they induce mass transport. This dual behaviour of gas bubbles raises the question what determines the balance between positive and negative impacts of gas bubbles in electrolyzers, and how we can leverage this. The pivotal factor seems to be *movement*:

- *Stagnant bubbles* whether on the electrode, membrane, or inside a porous support have a negative effect on electrolyser performance. These stagnant bubbles block the transport of ions, water, or electrons, and hence will result in extra resistance (both ohmic and mass transport resistance).
- *Moving gas bubbles* either through the pores of an electrode, or rising in the electrolyte positively affect the cell performance. By moving, gas bubbles displace electrolyte and create additional convection. This bubble-induced convection breaks diffusion boundary layers in the electrolyser and hence will result in improved mass transport.

To discuss the effects and potential of gas bubbles in electrolysers, I will address the following two questions, while answering the research questions (RQ) discussed in the introduction:

- How can we minimize the effects of stagnant bubbles in electrolysers?
  - **RQ1:** How large is the effect of gas bubbles on the cell voltage in a zero-gap alkaline water electrolyzer?
  - **RQ2:** How much can the cell voltage be reduced when gas-bubbles are removed from a zero-gap alkaline water electrolyzer with a pressure swing (5-180 s, 1-2 bar)?

- How can we optimally benefit from moving gas bubbles?
  - **RQ3:** What fluorescent pH probe is suitable to study mass transport at a gas-evolving electrode with Fluorescent Lifetime Imaging Microscopy (FLIM)?
  - **RQ4:** What microprocesses during gas bubble evolution are the biggest contribution to bubble-induced mass transport at electrodes?
  - **RQ5:** How much can the limiting current density of aqueous CO<sub>2</sub> reduction be improved with fast pressure pulses (50 Hz, 1-2.5 bar)?

After answering these questions, I will reflect on the role of gas bubbles in electrolysers with the following question:

Should we optimize bubble dynamics or aim for bubble-free systems?

#### HOW CAN WE MINIMIZE THE EFFECTS OF STAGNANT BUBBLES IN ELECTROLYSERS?

For alkaline water electrolyzers, and in particular zero-gap configurations (Chapter 2), quantifying the effects of gas bubbles is challenging. This is because electrolysers are usually only benchmarked by the cell voltage, in which all the losses are included into one number. A fast pressure pulse provides a solution here, as it allows for a comparison of an electrolyzer with and without bubbles. Virtually all bubbles are removed after a pressure pulse, while other parameters (such as materials, flow rate, and current density) remain the same.

**RQ1:** How large is the effect of gas bubbles on the cell voltage in a zero-gap alkaline water electrolyzer? The pressure swing measurements show that the overpotential due to bubbles ( $\eta_{\text{Bubbles}}$ ) scales linearly with current at low current densities (<150 mA cm<sup>-2</sup>), suggesting that the primary influence of bubbles on an alkaline electrolyser is ohmic in nature. For Ni perforated plate electrodes, the resistance is 0.3  $\Omega$  cm<sup>2</sup>, while for Ni foam electrodes, the resistance is 1.8  $\Omega$  cm<sup>2</sup> both in 1 M KOH, 30 °C. Like other ohmic resistances, bubble resistance is inversely proportional to the conductivity, which allows us to extrapolate the resistances to operating conditions relevant for industrial alkaline electrolysers (6M KOH, 80 °C). The bubble resistance for perforated plate electrodes, at these conditions is 0.051  $\Omega$  cm<sup>2</sup>. Using a typical industrial current density of 300 mA cm<sup>-2</sup>,  $\eta_{\text{Bubbles}}$  will be 15 mV for alkaline electrolysers. PEM electrolysers also suffer from bubbles, mostly due to mass transport limitations, the resulting  $\eta_{\text{Bubbles}}$  is about 40 mV at 1 A cm<sup>-2</sup> (ref[1]).

Using this, we can estimate the global electricity losses due to electric bubbles in 2030. By this year, the planned electrolyser capacity for green hydrogen is 560 GW[2]. At the time of writing this thesis, both PEM and alkaline electrolysers are commonly applied. By assuming a future 50%/50% split between PEM and alkaline water electrolysers, the total losses due to bubbles could reach up to 9.20 GW (Figure 6.1A). While this represents only a small fraction of the total electrolysis output, it is an enormous amount of energy. To put this into perspective, these losses would exceed the total installed electrical power of the Czech Republic in 2023 (~6.5 GW)[3]. I believe that addressing the stagnant bubble problem is strongly relevant in accelerating the energy transition.



Figure 6.1: Estimated bubble losses, assuming green water electrolyser targets of 2030 are met, assuming a 50% PEM, 50% alkaline split. The cell voltage was taken from IV curves of Hodges et.al.[4] Calculations are available in 6.1.1.

**RQ2:** How much can the cell voltage be reduced when gas-bubbles are removed from a zero-gap alkaline water electrolyzer with a pressure swing (5-180 s, 1-2 bar)? We have demonstrated that the effects of gas bubbles can be mitigated to an extent by applying pressure swings to an electrolyser. For a zero-gap electrolyser with Ni Foam electrodes (200 mA cm<sup>-2</sup>, 1 M KOH, 30 °C), this reduced cell voltage by up to 0.1 V. Regrettably, I believe that the additional energy costs for constant re-pressurization of the system, engineering challenges and safety risks of this approach, make successful implementation in an industrial-scale water electrolyser challenging.

While active bubble removal with a pressure swing poses challenges, passive bubble mitigation could be a viable alternative. During the pressure swing experiments, I observed the strong relationship between  $\eta_{\text{Bubbles}}$  and the geometry of the electrode. A foam electrode, which traps gas bubbles, results in a six times higher bubble resistance compared to a perforated plate electrode, which has sufficiently large pores to allow bubbles to escape. With emerging technologies such 3D printing and computational topology optimization, it should be possible to calculate and manufacture the ideal electrode geometry. I hypothesize that these electrodes will have sufficiently large pores and flow-through characteristics to facilitate effective bubble removal.

A challenge for optimizing electrode geometries is establishing a reliable method for deconvoluting effects of bubble coverage from other geometry aspects (such as surface area and tortuosity). A crucial parameter for this is bubble coverage ( $\theta$ ), which indicates the fraction of the electrode surface that is blocked by gas bubbles[5]. Traditionally, bubble coverage is measured optically on horizontal electrodes without flow. An under-explored alternative is to leverage the double layer capacitance (*C*). I performed some initial tests to show that this method works (Figure 6.2A and B, 10% lower capacitance for  $\theta = 10\%$ ). We should be able to measure  $\theta$  in situ and in operando using electrochemical impedance spectroscopy (EIS), provided we can accurately extract *C* from the constant phase element. This should greatly speed up the optimization of electrode geometries and operating conditions for good bubble management.



Figure 6.2: A. Photo of the capacitance measurements, air bubbles were placed with a pipette on the Ni foil surface until  $\sim 10\%$  of the surface was covered. B. Measurement of the double layer capacitance (*C*) of two Ni foil electrodes in 2 M KCl. *C* was measured by performing cyclic voltammetry (CV) at different scan rates (*S*). The y-axis shows the current of the CV curve at 0 V during the forward and backward scans. Data and corresponding CV curves are in 6.1.2.

#### HOW CAN WE OPTIMALLY BENEFIT FROM MOVING GAS BUBBLES?

After bubbles detach from the electrode, they become advantageous moving bubbles that contribute to the mass and heat transport in electrolyzers. To illustrate the importance of this transport: the world's largest green hydrogen project (260 MW alkaline electrolysis plant) is currently not fully operational due to issues with gas crossover[6]. Dr. M.T. de Groot (TU/e) commented the following on LinkedIn:

Gas crossover is a point of concern for pressurized alkaline electrolyzers and can seriously affect their flexibility. We did some research on the topic showing that there are ways to mitigate this. Yet, more research is needed. My suggestion would be to do this at labscale and not at 260 MW-scale.

The research he is referring to shows that gas crossover can be reduced by creating an electrode-diaphragm gap. When this gap is large enough, gas bubbles can move through this gap, absorb gasses from the oversaturated electrolyte solution, and transport them out the electrolyser. This can reduce the transport of dissolved gases across the di-aphragm[7]. This modification emphasizes the importance of understanding bubble induced mass-transport.

However, the understanding of bubble induced mass transport in electrolysis is not a new problem, and even the most recent mass transport coefficient equations make use of results from the 40-80's.[8–10] The existing relations are typically fitted to boundary layer experiments, which provide statistically robust data but require simplified assumptions about the underlying processes.[8, 11] The contributions of certain factors, such as bubble coalescence and Marangoni convection, remain poorly understood and are largely speculative at this point.[8, 12, 13] I believe we need to tackle this problem with new and out-of-the-box investigation methods. The researchers of the 40-80's were also competent; had the solution been straightforward, then they would have resolved it by now with existing methods. To that end, in operando optical measurements of flow and mass transport could facilitate the understanding of bubble phenomena. An upcoming and promising technique in this class is Fluorescence Lifetime Imaging Microscopy (FLIM). To my knowledge, this technique has only been sparsely applied to study mass transport, with the earliest reports dating back to just 2013.[14–19] Since FLIM is self-referencing, experiments can be set up quickly. However, the majority of FLIM research has been performed on biological systems, and hence little probes are existing for conditions relevant for  $CO_2$  or water electrolysis.

**RQ3:** What fluorescent pH probe is suitable to study mass transport at a gas-evolving electrode with FLIM? In Chapter 3 we have shown that Quinolinium-based probes open up pH measurements from 5 to 13.5. With FLIM we measure at a microscopic scale (4  $\mu$ m), at a temporal resolution of 3 fps. Using these probes, we investigated the mass transport in water and CO<sub>2</sub> electrolysers.[20] Additionally, I have tested additional molecules after the publication of our probe paper that will extend this pH range beyond 5-13.5 (Figure 6.3).



Figure 6.3: Fluorescent lifetime ( $\tau$ ) of two pH probes, that have potential to increase the pH range of FLIM even further, measurement method is identical to Chapter 3. A. Perylene-bis-anhydride (PBA) up to pH 14.5 B. Quinolinium probe QB21 up to pH 3. Data is available in 6.1.3.

**RQ4:** What microprocesses during gas bubble evolution are the biggest contribution to bubble-induced mass transport at electrodes? Using FLIM and  $\mu$ PIV, we have shown that bubble detachment and wake flow are the main drivers of bubble-induced mass transport. However, these experiments were still at a limited range of relatively low current densities (1-20 mA cm<sup>-2</sup>). Experiments at a larger range of current densities should allow us to compare the mass transport to theoretical and numerical models, for example from the Haverkort group.[8] FLIM is also expected to perform well at higher current densities, which could provide insights into, for example, the role of bubble coalescence in mass transport.

**RQ5:** How much can the limiting current density of aqueous CO<sub>2</sub> reduction be improved with fast pressure pulses (50 Hz, 1-2.5 bar)? A good design of electrolyser and electrode has shown to enhance the effects of bubble-induced mass transport.[7, 21–23] In Chapter 5, I have demonstrated that process intensification can amplify these effects even further. By applying fast pressure pulses that cause bubbles on the electrode to vibrate, we achieved partial CO<sub>2</sub> reduction (CO<sub>2</sub>R) current densities of 89 mA cm<sup>-2</sup>—an order of magnitude higher than systems relying solely on bubble-induced mass transport. Despite these promising results, fast pressure pulses may introduce new engineering challenges. For example, as a pulse generating system, we used vibratory pumps designed for an espresso machine as a last resort because we could not find a better system. Because these pumps were operating continuously, instead of for a short duration in an espresso machine, the lifetime of the pumps in our device was only ~100 hours of operation. Moreover, the energy efficiency of these pumps is very low. Therefore, it would be required to develop new pressure pulse generating systems, i.e. vibratory pumps that are designed for continuous, more energy efficient operation.

#### SHOULD WE OPTIMIZE BUBBLE DYNAMICS OR AIM FOR BUBBLE-FREE SYSTEMS?

To make the adoption of green hydrogen viable, the technology will need to be cost competitive with traditional fossil-based resources. Figure 6.4A shows the levelized cost of hydrogen (LCOH) for a PEM and alkaline electrolyser, calculated for on-shore wind electricity in the Netherlands[24]. At these conditions 1 kg of alkaline hydrogen costs  $\in$ 5.33. One kg contains 33.3 kWh of energy, which makes the energy price 0.160  $\notin$  kWh<sup>-1</sup>, which is already in the same order of magnitude as the current energy price of gasoline 0.208  $\notin$  kWh<sup>-1</sup> (E10, Netherlands[25]). Note that typical combustion engines have a performance of, at most, 30%, whereas fuel cells should give, at least, 60%. This will make H<sub>2</sub> energy prices more favorable.

However, the green H<sub>2</sub> price does not include additional costs, like transport storage and certification yet, which can result in another 2-5  $\notin$ /kg added to the costs[26], or the high taxes (~45%) on gasoline. I believe a large cost reduction (>20%) is required to make green hydrogen cost-competitive. This is also needed to compete with grey H<sub>2</sub> which currently has a cost of ~2  $\notin$ /kg.[27]



Figure 6.4: A. Levelized cost of hydrogen (LCOH) in the Netherlands, based on-shore wind energy[24] This price does not include additional costs, like pressurization, profit margins and certification B. I/V curves of commercial alkaline and PEM electrolysers, compared to the novel capillary flow-fed electrolysis. Data source: Figure 3C of Hodges et.al.[4]

Good bubble management could reduce electricity costs and allow for higher cur-

rent densities, which in turn would lower the CAPEX. However, as already shown in Figure 6.1, it is unlikely that such improvements alone would lead to the required large cost reduction. This cost reduction will need to be tackled by bit by bit, for example by improvements in membranes/separators, catalysts, and the balance of plant (BOP). I believe both PEM and alkaline electrolysers will play important roles during the transition to green energy, but I believe technologies with a different approach have the potential to make much larger reductions of the LCOH.

For example, the Battolyser[28]—a technology that combines the functionalities of a battery and an electrolyser—could justify higher capital costs by offering more utility. Additionally, in 2022, a novel bubble-free electrolyser was introduced, utilizing capillary flow and a very thin porous diaphragm. As shown in Figure 6.4B, this system surpasses the energy efficiency of both commercial alkaline and PEM electrolysers, while simultaneously using earth-abundant materials and having easier BOP. This raises the question: should we consider going bubble-free? While this bubble-free design resolves the gas transport issue, it creates a water transport issue. The startup behind it is currently facing challenges with scaling up, because of the insufficient water transport to the catalyst. Even though electrolysis is a century-old, large-scale technology, new developments must show which pathways will make green hydrogen viable. I am excited for what the future will bring.

#### **6.1.** SUPPLEMENTARY INFORMATION

#### **6.1.1.** CALCULATION OF BUBBLE LOSSES

IEA predicts an installed green electrolyser capacity of 560 GW by 2030, when assuming a 50%:50% split between alkaline and PEM electrolysis, their total capacity will be 280 GW each by 20301. The losses caused by gas bubbles were calculated as follows:

$$P_{\text{loss-Bubbles}} = P \cdot \frac{\eta_{\text{Bubbles}}}{E_{\text{Cell}}}$$
(S6.1)

Here  $P_{\text{loss-Bubbles}}$  is the amount of power lost due to gas bubbles in GW, *P* is total electrolyser capacity in GW,  $\eta_{\text{Bubbles}}$  is the overpotential due to gas bubbles in V, and  $E_{\text{Cell}}$  is the cell potential of the process in V. For operating current densities I used 1 A cm<sup>-2</sup> and 0.3 A cm<sup>-2</sup> for PEM and alkaline respectively to have a comparable cell voltage.

Table S6.1: Electrolyser performance data used for calculating global losses due to gas bubbles

	P [GW][2]	$j [{\rm A}{\rm cm}^{-2}]$	E <sub>Cell</sub> [V]	$\eta_{\text{Bubbles}}$ [V]	Ploss-Bubbles [GW]
PEM	280	1	1.69 [4]	0.04 [1]	6.63
Alkaline	280	0.3	1.665[4]	0.015	2.57

#### **6.1.2.** DATA OF CAPACITANCE MEASUREMENTS



Figure S6.1: Cyclic voltammetry curves corresponding to capacitance in Figure 6.2 for a bubble coverage of A.  $\theta = 0$  and B.  $\theta = 0.1$ 

Table S6.2: Currents from the cyclic voltammetry curves at 0 V, averaged over 3 cycles. Currents did not deviate more than 2% over repeat cycles. These values were fitted with the trendline function of Excel to find the Capacitance in Figure 6.2B

Scanrate [mV/s]	Current, $\theta = 0 \ [\mu A]$		Current, $\theta = 0.1 \ [\mu A]$	
10	0.14	-0.13	0.15	-0.22
25	0.34	-0.20	0.24	-0.30
50	0.66	-0.68	0.82	-0.89
75	1.20	-1.21	1.18	-1.26
100	1.58	-1.56	1.52	-1.59
150	2.22	-2.21	2.10	-2.17
200	2.79	-2.78	2.60	-2.67
250	3.18	-3.19	2.92	-3.03
300	3.66	-3.64	3.32	-3.43
350	4.08	-4.08	3.67	-3.81
400	4.47	-4.47	4.03	-4.14
450	4.86	-4.84	4.38	-4.47
500	5.22	-5.20	4.66	-4.80

#### 6.1.3. DATA OF FLIM PROBES

Table S6.3: pH-Lifetime data for FLIM probes PBA and QB21

	PBA			QB2	1
pН	$\tau_{\phi}$ [ns]	Stddev [ns]	pH	$\tau_{\phi}$ [ns]	Stddev [ns]
11.5	5.53	0.22	4.02	6.23	0.34
12.063	5.62	0.23	3.55	7.95	0.38
12.464	5.71	0.23	3.04	8.54	0.38
12.439	5.71	0.23	2.75	8.68	0.39
12.75	5.67	0.22	2.55	8.73	0.39
13.005	5.61	0.22	2.25	8.75	0.38
13.256	5.51	0.22	2.03	8.76	0.38
13.502	5.45	0.21	1.75	8.74	0.39
13.756	5.4	0.22	1.5	8.72	0.38
13.908	5.34	0.22	1.25	8.68	0.39
14.02	5.27	0.22	1.08	8.63	0.39
14.16	5.19	0.21			
15.02	4.65	0.41			

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## LIST OF PUBLICATIONS

Journal articles included in this thesis:

- Jorrit Bleeker, Florianne M. Wiegel, Aron P. Kahn, J.W. (Willem) Haverkort, Christiaan V. Schinkel, Maxime Hoogland, Lorenz M. Baumgartner, Wolter F. Jager, J.R. (Ruud) van Ommen, David A. Vermaas. Bubble-induced mass transport at vertical hydrogen evolving electrodes *In preparation* (2024)
- Jorrit Bleeker, Lisanne C. Bakker, Sue S.J. van Deursen, Timo J.J.M. van Overveld, Katie M.R. Lawrence, Isabell Bagemihl, Giacomo Lastrucci, Duco Bosma, Christiaan V. Schinkel, Evert C. Wagner, J.R. (Ruud) van Ommen, David A. Vermaas. Pressure-Pulsed Flow Triples Mass Transport in Aqueous CO<sub>2</sub> Electrolysis Submitted (2024)
- 2. **Jorrit Bleeker**, Celine van Kasteren, J.R. (Ruud) van Ommen, David A. Vermaas. Gas bubble removal from a zero-gap alkaline electrolyser with a pressure swing and why foam electrodes might not be suitable at high current densities *International Journal of Hydrogen Energy* 57, (Feb 2024), 1398-1407.
- Jorrit Bleeker, Aron P. Kahn, Lorenz M. Baumgartner, Ferdinand C. Grozema, David A. Vermaas, Wolter F. Jager. Quinolinium-Based Fluorescent Probes for Dynamic pH Monitoring in Aqueous Media at High pH Using Fluorescence Lifetime Imaging *ACS Sensors 8*, 5 (Apr 2023), 2050–2059.

Journal articles outside this thesis:

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# **CURRICULUM VITÆ**

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