Using auxiliary electrochemical working electrodes as probe during contact glow discharge electrolysis: A proof of concept study

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Abstract

Plasma in-liquid by means of anodic contact glow discharge electrolysis (aCGDE) is a growing research field allowing the selective modification of the electrode and the electrolyte. The aim of this proof of concept study is to demonstrate that auxiliary electrochemical electrodes placed in vicinity to the plasma electrode, can be modified by aCGDE. Furthermore, we illustrate in how far such auxiliary electrodes can be used as a probe to detect products (in particular H₂, H₂O₂, and O₂) formed in the solution by aCGDE via electrochemical techniques. In this work aCGDE is achieved by applying a voltage of 580 V to a small Pt wire (plasma electrode) vs. a large stainless steel counter electrode. An auxiliary Pt electrochemical working electrode, operated in a three electrode configuration, is placed at different distances from the plasma working electrode. Depending on the distance, we find small changes in the electrode structure. More importantly, we will show that in principle the local H₂O₂ concentration in the electrolyte can be monitored operando. After aCGDE the concentration changes with time and depends on the distance from the plasma electrode.

Introduction

Studying plasma in-liquids has received increasing scientific interest over the last two decades for its possible application in, e.g., wastewater treatment,¹–⁵ nanoparticle formation,²,⁴,⁶–¹³ catalyst material preparation,¹⁴,¹⁵ plasma electrolytic oxidation,¹⁶–¹⁸ or plasma electrolytic polishing.¹⁹,²⁰ These investigations provide information on the modification of the plasma electrode or changes induced within the electrolyte. Gas-phase plasma can be used in a similar way to modify the plasma electrode or the properties of a substrate placed close to the plasma source. Related to catalytic applications, the gas-phase plasma can also be used, e.g., to change the mechanism of a catalytic reaction on the target (gas-phase plasma catalysis)²¹–²³ or to tailor the structural properties of the target, for example, to form catalyst materials with distinct (electro)catalytic properties.²⁴–²⁷ In contrast, much less is known about the effect of in-liquid plasma on target materials.

A better understanding of the impact of in-liquid plasma on an auxiliary target electrode placed in the same electrolyte in proximity to an in-liquid plasma electrode is of interest for the following applications. Firstly, in-liquid plasma could be used to prepare an electrocatalyst in situ. This approach would have the advantage that the electrodes do not have to be trans-
ferred after the plasma treatment from a gas-phase atmosphere into an electrochemical cell, avoiding contamination or uncontrolled restructuring of the electrode. Furthermore, the electrode potential of the auxiliary electrode can be changed during the preparation process, allowing for more specific tailoring of its structural properties. Secondly, an auxiliary electrode could be used as an electrochemical probe to determine the species formed by the plasma in the electrolyte, to measure the solution pH, or the voltage drop in the electrolyte.

Such fundamental aspects have, to the best of our knowledge, so far not been considered in the ongoing research, but are vital in the search of possible applications. The purpose of this work is to illustrate the influence of plasma in-liquid on the current–voltage behavior of an auxiliary electrode in solution placed in proximity of the plasma electrode and whether this auxiliary electrode can be used to determine products formed during the plasma. In general, plasma in-liquid can be generated by different approaches.\(^7,28\) Here, we focus on anodic contact glow discharge electrolysis (aCGDE), which is achieved by applying a high voltage between a gas evolving electrode and a significantly larger counter electrode.\(^29–33\) Here, Pt is used as plasma working electrode (PWE), since it was suggested to be stable under these conditions.\(^15,30,31,34–37\) The auxiliary electrochemical working electrode (AE) is also made of Pt, which is an intensively studied electrochemical electrode material\(^38–43\) and therefore an optimal benchmark system. Also, considering the key products that form concomitantly during aCGDE are H\(_2\), O\(_2\) and H\(_2\)O\(_2\),\(^30,34,44\) the electrocatalytic reaction of these species with Pt electrodes in alkaline electrolyte are also described in detail in the literature.\(^45–50\) A key aspect is the detection of H\(_2\)O\(_2\), which is usually determined after the electrolysis by means of titration.\(^30,51–53\) This approach does, however, not provide any information on the spatial distribution or temporal evolution of the H\(_2\)O\(_2\) formed during aCGDE. Other methods are able to circumvent this issue to some extend.\(^22,23\)

In total, knowing about local concentrations is for example important to understand possible structural changes of the working electrode induced by the H\(_2\)O\(_2\) after aCGDE.\(^15\) In the field of electrochemistry Pt is used as collector electrode, which oxidizes H\(_2\)O\(_2\) selectively, i.e., during the oxygen reduction reaction (ORR).\(^54–56\) As a proof of concept, in this work a Pt wire is placed as H\(_2\)O\(_2\) probe at different distances from the PWE.

## Results and discussion

The experiments were performed in a large cylindrical glass cell containing 0.01 M KOH. The two electrodes for aCGDE (PWE and plasma counter electrode - PCE) and the three electrochemical electrodes (auxiliary electrode - AE, reversible hydrogen electrode - RHE, and electrochemical counter electrode - ECE) are immersed in the cell as shown in the schematic illustration in Fig. 1. A glass tube is placed around the plasma counter electrode to remove volatile products created at the PCE.\(^30\) In our studies, the AE was placed at a distance of either 1.5 cm or 4.5 cm from the PWE. The applied voltage between the PWE and the PCE is given in V, while the potential at the AE is given on the RHE scale (V\(_{\text{RHE}}\)). A detailed description of the experimental set-up, materials used and experimental procedures is provided in the experimental section.

![Figure 1: Schematic illustration of the electrochemical cell including the plasma electrodes (PWE and PCE) and the electrochemical electrodes (AE, ECE, and RHE). See text for details.](image-url)
The effect of aCGDE on the AE was studied by comparing the variation of electrode potential ($E$) vs. time ($t$) (Fig. 2 top row) with the current density ($j$) vs. $t$ (Fig. 2 middle and bottom row). Each experiment consists of a combination of the following experimental steps:

Step A: Cyclic voltammetry (measuring the current response while applying a triangular wave potential) recorded at 50 mV s$^{-1}$ between 0.0 and 1.05 V_RHE in the absence of aCGDE, followed by both or either one of the following steps B.

Step B1: Keeping the AE at 1.0 V_RHE (unless otherwise mentioned) during 30 s of aCGDE (PWE anode at 580 V vs. a stainless steel cathode).

Step B2: Keeping the AE at 1.0 V_RHE for 15 min in the absence of aCGDE.

Step C: Recording cyclic voltammograms (CVs) between 0.00 and 1.05 V_RHE in the absence of aCGDE.

Each column in Fig. 2 represents one of the experimental steps above. The time axis always counts from the beginning of each of these steps. The variation of the current density for an AE located 1.5 cm from the PWE (close to the PWE) is shown as a red curve and that for a distance of 4.5 cm as a blue curve (far from the PWE). The green curve represents the case where the AE was not exposed to aCGDE (no step B1), and was kept for 15 min at 1.0 V (in step B2). The same color scheme is used throughout the article. After aCGDE, a waiting period of 15 min was applied to ensure that the species formed by the plasma have sufficient time to distribute evenly in the electrolyte.

For all experiments the potential-dependent variation of current density vs. time in step A is almost identical (Figs. 2e and i), indicating that the experimental conditions at the start of each experiment are the same. This is even more apparent by comparing the current density vs. potential curves in Fig. S1. The voltammetric features apparent in these curves are discussed further below.

Performing aCGDE while applying a constant potential at an AE placed close to the PWE (step B1: Figs. 2f and j red curves), a large negative current density is recorded at the AE. The current density is several orders of magnitude larger compared to the redox currents obtained without aCGDE in step A. In contrast, much less negative current densities are recorded when the AE is placed far from the PWE (blue curves). We assume that the voltage drop between the PCE and PWE changes the electrolyte potential not only between the plasma electrodes but also further away from these electrodes in the electrochemical cell. Hence, depending on the position of the electrochemical electrodes, the potential at the AE cannot be controlled properly. In addition, the currents recorded between the PWE and PCE are fluctuating strongly, which induces changes in the electric field and in turn induces a strong noise in the current densities recorded at the AE in step B1. Note that the effect of electric fields on auxiliary electrodes is not unknown and is for example explored in ohmic microscopy and bipolar electrochemistry. Overall, to derive a more meaningful conclusion, the effect of voltage drop on auxiliary electrodes will be discussed elsewhere using an electrochemical cell with a more defined geometry, which also allows a more precise positioning of the different electrodes.

In step B2, the plasma was turned off and the AE potential was kept for 15 min at 1.0 V_RHE (Fig. 2g). When the AE is located far away from the PWE, the current density (blue curve) recorded at the AE is almost zero and remains constant for the rest of the waiting period. In the case where the AE is located close to the PWE the current density (red curve) is high when the plasma is turned off. With time, the current density decreases and remains constant at slightly positive current densities during the entire waiting time. For comparison, keeping an AE at 1.0 V_RHE for 15 min without exposing it to aCGDE (no step B1 - green curve in Fig. 2g), the current density is almost zero. This difference in current densities recorded at the AE placed at different distances from the PWE, demonstrates that aCGDE certainly has...
Figure 2: Effect of aCGDE on the AE by comparing the variation of the electrode potential ($E$) vs. time ($t$) (top row) on the current density ($j$) vs. $t$ (middle and bottom row). The middle row shows the sequence of experimental steps A, B1, B2 and C, whereas the bottom row only comprises steps A, B1 and C. Each column represents the experimental steps described in the main text. Steps A, B2, and C are performed without aCGDE. In step B1, simultaneously aCGDE was performed at 580 V for 30 s. The red and blue curves show the measurements for AEs placed at a distance of 1.5 cm or 4.5 cm from the PWE, respectively. For comparison, the green curve shows the case where the AE was not exposed to aCGDE (no step B1).

an impact on the current time profiles recorded at auxiliary electrodes.

After the chronoamperometry steps (B1 and B2 or only B2), cyclic voltammetry was performed at the AE in step C (Figs. 2h and l). Overall, the evolution of current densities, especially in the first few seconds of the first cycle, strongly depends on the waiting time as well as on the position of the AE with respect to the PWE during aCGDE. These features and current density variations can be due to changes induced by the plasma or waiting time on the AE and the reaction of species from the electrolyte formed during aCGDE on the AE surface.

As described above, the key products that form concomitantly during aCGDE are H$_2$, O$_2$ and H$_2$O$_2$, whose electrocatalytic properties with Pt electrodes are well described in literature. In order to assess whether or not the features observed in Figs. 2h and l are related to the presence of these species in solution after aCGDE, we performed a separate set of cyclic voltammetry measurements in electrolytes saturated with either one of the reactants possibly formed during aCGDE, shown in Fig. 3a. The grey curve shows the cyclic voltammogram (CV) of Pt recorded in N$_2$ saturated 0.01 M KOH, the light blue curve in O$_2$ saturated 0.01 M KOH, the pink curve in H$_2$ saturated 0.01 M KOH and the orange curve in 0.01 M KOH containing H$_2$O$_2$. Additional measurements with a larger upper potential limit...
are shown in Fig. S2. All CVs were recorded at a scan rate of 50 mV s\(^{-1}\).

In brief, these CVs can be interpreted as follows. The CV recorded in N\(_2\) saturated 0.01 M KOH (grey curve) shows the onset of HER at \(E < 0.05\) V\(_{\text{RHE}}\), features for the ad-/desorption of hydrogen between 0.05 V\(_{\text{RHE}}\) and 0.5 V\(_{\text{RHE}}\) (which are sensitive to changes in surface crystallographic orientation), and the ad-/desorption of hydroxyl or oxide formation/reduction at \(E > 0.8\) V\(_{\text{RHE}}\).\(^{42,64}\) The slightly negative current densities for \(E < \text{ca. } 0.95\) V in this grey curve are caused by the reduction of residual O\(_2\) in the electrolyte (ORR). Similar CVs to the grey curve are also obtained for all electrodes investigated before aCGDE in step A shown in Fig. S1.

In H\(_2\)-containing 0.01 M KOH (pink curve), the positive current density between 0.05 V and 1.0 V is attributed to the hydrogen oxidation reaction (HOR), which is inhibited in the region of surface Pt oxide formation at around \(E > 0.95\) V. In O\(_2\)-containing 0.01 M KOH (light blue curve) the negative current density at \(E < \text{ca. } 0.95\) V is related to the ORR. In H\(_2\)O\(_2\)-containing 0.01 M KOH (orange curve) the negative current density at around \(E < 0.95\) V is related to the hydrogen peroxide reduction reaction (HPRR), and the positive current density at around \(E > 0.95\) V is related to the hydrogen peroxide oxidation reaction (HPOR). In all cases, the ad-/desorption features observed in the CV recorded in N\(_2\)-saturated 0.01 M KOH (grey curve), overlap with the current density related to the electrocatalytic reactions. In contrast to literature findings, the here reported current densities are low due to limited diffusion of the reactants to the electrode under stagnant electrolyte conditions.\(^{45-47,497,50}\)

Figures 3b and c show the CVs from Figs. 2h and l (step C) recorded after aCGDE with and without waiting time, respectively. Similar results are also obtained when a lower voltage is applied between the PWE and the plasma counter electrode (550 V in Fig. S3), as well as with and without shielding the plasma counter electrode by a glass tube (Fig. S4). In addition, for comparison, a CV recorded in step A

Figure 3: a) Cyclic voltammograms of a Pt wire recorded at 50 mV s\(^{-1}\) in 0.01 M KOH a) either saturated with N\(_2\) (grey), H\(_2\) (pink), O\(_2\) (light blue) or after addition of H\(_2\)O\(_2\) (orange). b) and c) shows the data from Figs. 2h and l (step C) with the same color code for the individual measurements. CVs recorded in non-deaerated electrolyte before (black) and after aCGDE for 30 s at 580 V (red and blue). The red curve shows the first half cycle after the plasma at a distance of 1.5 cm from the PWE and the one in blue at a distance of 4.5 cm, respectively. Panel b) shows the CVs obtained after performing the experimental steps B1 and B2 and c) after step B1 (no step B2). The green curve in b) and c) shows the current density voltage response after 15 min waiting at 1.00 V, without applying aCGDE before.
(before the aCGDE treatment) is included in black and a CV recorded after 15 min waiting time without applying aCGDE in green.

Comparing the black and the green curves (before and after holding the potential at 1.0 V<sub>RHE</sub> for 15 min) in Figs. 3b and c, a larger reduction current is apparent in the green curve in the first negative going scan at around 0.8 V<sub>RHE</sub>. This feature is related to the degree of electrode oxidation at high potentials. In general, the size of the reduction peak depends on the upper potential limit of the CV as well as on the time and potential at which the electrode is kept (see also Fig. S5). Hence, the larger reduction peak in the green curve is caused by holding the potential at 1.05 V for 15 min.

Cyclic voltammograms recorded on the AEs placed at different distances from the PWE, after aCGDE and subsequent waiting time at 1.0 V<sub>RHE</sub> (steps B1 and B2) are shown in Fig. 3b. The CV recorded on an AE close to the PWE (red curve) is almost identical to the green curve (obtained without applying aCGDE). On the other hand, if the AE is placed further away from the PWE (blue curve), the size of the reduction peak in the first negative going scan is larger and shifted to more negative potentials (0.65 V<sub>RHE</sub>) compared to the red and green curves. This implies that the electrode is significantly more oxidized. As mentioned above, such an effect would be expected for longer waiting times or if the upper potential limit was higher (see Fig. S5 and more details below).

Skipping the waiting time after aCGDE and recording CVs directly thereafter (only step B1) for AEs placed at different distances from the PWE are shown in Fig. 3c. For AEs close to the PWE (red curve), in the first negative going scan a large positive current density is observed at high potentials (0.8 – 0.95 V<sub>RHE</sub>). The current density decreases at more negative potentials until at ca. 0.5 V<sub>RHE</sub>, the curve follows the CV recorded before aCGDE (black curve). Compared to the CVs presented in Fig. 3a, this large positive current density can at least at high potentials (> 0.95 V) be attributed to the oxidation of H<sub>2</sub>O<sub>2</sub>. Note that the HOR and the
ORR are almost suppressed at these potentials, as shown in Fig. 3a and Fig. S2. The H$_2$O$_2$ oxidation current is also measured at higher potentials (above 0.95 V$_{RHE}$) in the following potential cycles, as shown in Fig. S6. The temporal decrease of the positive current density is more clearly seen in the potentiostatic measurements in Fig. 2g (red curve). The CVs and the potentiostatic experiments indicate that the H$_2$O$_2$ remains in the region around the AE for a certain time until it dissipates into the electrolyte or reacts with the Pt PWE to decompose into O$_2$ and H$_2$O.$^{66,67}$

For AEs located farther from the PWE (blue curve), such a positive current density is not observed in the first negative going or subsequent scans, indicating that H$_2$O$_2$ is not measurably present in the electrolyte far away from the PWE. Similar to the blue curve in Fig. 3c, obtained directly after aCGDE, a large reduction peak is observed at around 0.65 V$_{RHE}$ in the first negative going scan in Fig. 3b (steps B1 and B2). This large peak, which is observed in both experiments, suggests that the electrode surface oxidizes significantly during aCGDE. Interestingly this suggests, that the plasma or the species formed by the plasma only affect the structural properties of the Pt AE, when the AE is placed far away (4.5 cm) from the PWE. For the time being it is not clear if the increase in Pt oxide formation is induced (i) by the plasma (or plasma species) or whether it is related (ii) to changes in electrode potential induced by the electric fields during aCGDE, which could cause an uncontrolled oxidation of the electrode during aCGDE.

Overall, our measurements indicate that the plasma or the species formed by the plasma do not have a significant impact on the structural properties of the Pt AE. The additional current densities in the CVs, with respect to a CV recorded in N$_2$ saturated 0.01 M KOH (see black curves), are therefore attributed to the reaction of the Pt AE with the species formed by the plasma in the solution, where the reaction rates depend on the product distribution and its temporal evolution in the electrolyte. When the AE is located close (1.5 cm) to the PWE, significantly different current densities arise at the AE directly after aCGDE, which are tentatively attributed to the reaction of plasma created species (H$_2$, O$_2$, H$_2$O$_2$) with the Pt AE. In the CVs recorded right after aCGDE (step B1) and at potentials < 0.65 V$_{RHE}$, a more significant negative current density is observed. Assigning these current densities to the reaction of different species with the Pt AEs is not straightforward, since the total current density is a sum of HOR current density (positive), ORR current density (negative), HPRR current density (negative) and surface redox processes. At high electrode potentials, especially 1.0 V$_{RHE}$, the situation is more clear. The observed positive current density can basically only be attributed to the oxidation of H$_2$O$_2$, with minor contributions from the oxidation of H$_2$. These positive current densities persist after multiple cycles (see Fig. S6). Finally, the different behavior of the $j$ vs. $E$ curve in the first negative going scan of the CV recorded after aCGDE for AEs placed at different distances from the PWE suggests that the product distribution in the solution changes with the distance from the PWE. The change in current density in Fig. 2g during the waiting time after aCGDE also implies that the product distribution changes with time.

## Conclusion

In this work we elucidated to what extend auxiliary electrochemical working electrodes can be used to determine by electrochemical methods the impact of aCGDE on (i) the structural properties of an auxiliary electrode and (ii) in how far such electrodes can be used as a probe to detect products formed during and after aCGDE. In both cases it was not yet possible to determine these properties during aCGDE. We suggested that changes in the electrode potential of the electrochemical electrodes might be responsible for this observation. This issue has to be addressed more specifically in a more detailed study where the electrode and electrochemical cell geometries are more defined. After the aCGDE we were able to detect qualitatively the presence of H$_2$O$_2$ which was sug-
gested to be formed during aCGDE. The concentration in the electrolyte depends on the distance from the electrode as well as on the waiting time after electrolysis. This proof of concept study demonstrates that an electrochemical probe can indeed be used to determine the H$_2$O$_2$ concentration operando and also locally in the electrolyte, which is so far not accessible with other techniques. Overall, such information is crucial for further studies aiming at a more detailed understanding of product formation during aCGDE, the composition of the plasma, the structure formation processes at the plasma electrode or the reaction of these intermediates with species in the electrolyte.

**Experimental**

All experiments were performed in a five electrode setup. This consisted of a classical three electrode setup usually used for electrochemical measurements with an auxiliary electrochemical working electrode (AE), a reference electrode (here a reversible hydrogen electrode - RHE) and an electrochemical counter electrode as well as two electrodes to generate a plasma in-liquid, namely a plasma working electrode (PWE) and a plasma counter electrode (PCE).

**Materials:** Pt wires with a diameter of 0.5 mm and a purity of 99.99 % from MaTecK were utilized as AE and PWE. As electrochemical counter electrode a Pt-sheet (10 × 7.5 mm) and as plasma counter electrode a stainless steel plate (20 mm × 20 mm × 3.5 mm size) were used, respectively.

The 0.01 M KOH solution was prepared from KOH pellets (99.99 %, Sigma-Aldrich) and Milli-Q water (18.2 MΩ cm, TOC ≤ 3 ppb).

**Sample preparation:** For the first measurement of each day, the Pt wires were annealed for 3 min in a propane (MTI) flame atmosphere. Since previous studies suggested that the Pt wire electrodes do not change measurably under our experimental conditions, the wires were not freshly prepared for the subsequent measurements on the same day.

**Electrochemical Cell** In order to study the influence of the PWE on the AE, all electrodes were placed in the same electrochemical cell. The latter consists of a large glass beaker (diameter: 13.5 cm, height: 7.5 cm) containing 650 mL of 0.01 M KOH, where a glass tube was placed around the plasma counter electrode (illustrated in Fig. 1). In the case where no glass tube was employed (as in the measurements shown in Fig. S4) the beaker was only filled with 500 mL electrolyte.

The Pt wire used as PWE was protected at both ends with polymer caps (fabricated from Eppendorf pipette tips). The cap around the wire apex is necessary to prevent the wire from melting during aCGDE. The caps were adjusted such that 2 mm of the wire are exposed to the electrolyte (surface area of 0.031 cm$^2$). The PWE and plasma counter electrode were placed between 1.2 cm to 1.5 cm apart from one another.

The voltage between these electrodes was applied with a TDK-Lambda Power Supply (630 V / 1.365 A). The power supply was controlled with a LabView program. Unless otherwise mentioned, 580 V were applied for 30 s between the PWE and plasma counter electrode. At this voltage the plasma ignites immediately, as compared to lower voltages.

The Pt wire used as AE was immersed 10 mm in the electrolyte solution, where the distance was controlled by putting a protective polymer cap (see above) at the upper end of the wire (surface area of 0.159 cm$^2$). In this case the apex of the wire does not need special protection, since the current densities are much lower compared to those recorded at the PWE. A home-made and freshly prepared reversible hydrogen electrode (RHE) was used as reference electrode. The potential at the AE was controlled with a FHI ELAB potentiostat. All potentials are given on the RHE scale (V$_{\text{RHE}}$).

**Experimental Procedure** Since the aCGDE experiments lead to an accumulation of products in the solution, namely H$_2$, O$_2$ and H$_2$O$_2$, the electrolyte was changed after each experiment to have the same initial conditions for all experiments. To reduce the possible impact of H$_2$ formed at the plasma counter electrode during aCGDE on the other electrodes (especially the AE), a glass tube was placed around the elec-
trode, allowing the majority of the formed H\textsubscript{2} to leave the electrolyte within the perimeter of the glass tube.\textsuperscript{30}

All measurements were carried out at room temperature. The temperature of the electrolyte before and after the experiment was very similar in each case, with ca. 24 \degree C measured with a thermometer immersed in the solution. Note that after aCGDE the temperature in the electrolyte is rather inhomogeneous, with higher electrolyte temperatures around the PWE. Since the formation of O\textsubscript{2} during aCGDE is inevitable, the electrolyte was not deaerated before the experiments. All experiments were performed without stirring the electrolyte.

For the electrochemical characterization, CVs were recorded before and after aCGDE. The initial potential for all measurements (unless otherwise mentioned) was set around the open circuit potential (ca. 1.00 V\textsubscript{RHE}), the lower potential limit to 0.00 V\textsubscript{RHE} and the upper potential limit to 1.05 V\textsubscript{RHE}. For some measurements the upper potential limit was increased to 1.25 V\textsubscript{RHE}. When the upper potential limit was increased to 1.25 V\textsubscript{RHE}, the initial potential was set to 1.20 V\textsubscript{RHE}. The scan rate for all measurements was 50 mV s\textsuperscript{-1} and the initial scan rate was always negative (negative potential scan). During the aCGDE in step B1 and in step B2 the potential of the AE was held at the initial potential (1.00 V\textsubscript{RHE}).

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**Keywords**

Contact Glow Discharge Electrolysis, Platinum, Hydrogen Peroxide, Electrocatalysis

**TOC Figure and Text**

The influence of anodic contact glow discharge electrolysis on a Pt auxiliary electrode in alkaline electrolyte was investigated as a function of the distance between the electrodes and time. By studying the electrochemical properties of Pt before, during and after aCGDE by cyclic voltammetry, we demonstrate that the Pt auxiliary electrode can be used to monitor operando the formation of H\textsubscript{2}O\textsubscript{2} by aCGDE in the electrolyte. The concentration depends on the distance of the electrodes to each other and the detection time.
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SUPPORTING INFORMATION -
Using auxiliary electrochemical working electrodes as probe during contact glow discharge electrolysis: A proof of concept study

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**S1: Reproducibility of the starting conditions**

Figure 1 shows a set of CVs of the Pt wire AE recorded in 0.01 M KOH at a scan rate of 50 mV s\(^{-1}\) obtained in step A (see manuscript). Each curve represents a new measurement. All CVs look almost alike, indicating that the experimental conditions (structural properties of the electrodes and electrolyte purity) are similar in each experiment.

![Figure 1: Set of CVs of Pt wire AEs recorded in 0.01 M KOH at a scan rate of 50 mV s\(^{-1}\), obtained in step A (see manuscript) for different experiments.](figure1.png)
**S2: Influence of upper potential limit on electrocatalytic properties**

As discussed in the manuscript, H$_2$, O$_2$, and H$_2$O$_2$ are formed during aCGDE. The electrocatalytic reactions of these species with Pt, are depicted in the CVs in Fig. 2. These were recorded in 0.01 M KOH solutions, which were saturated with the respective reactants. A similar plot with a lower upper potential limit is shown in Fig. 3a and discussed in the manuscript.

![Figure 2: Pt CVs measured with a scan rate of 50 mV s$^{-1}$ in 0.01 M KOH saturated with N$_2$ (grey curve), O$_2$ (light blue curve), H$_2$ (pink curve) and admixed with H$_2$O$_2$ (orange curve).](image-url)
S3: Influence of the PWE voltage on the CV features recorded at the AE (550 V vs. 580 V)

Figure 3 shows the CVs of Pt electrodes recorded in 0.01 M KOH at a scan rate of 50 mV s$^{-1}$, where Fig. 3a shows the CVs recorded directly after aCGDE (step B1) and in Fig. 3b after aCGDE and waiting for 15 min (steps B1 and B2). The solid lines correspond to the data obtained by applying 580 V at the PWE (as in the manuscript) and the dashed lines by applying 550 V. At this lower voltage the plasma ignites only after a few seconds. Overall the curves look rather similar. We suggest that the shifts of the current density profiles are attributed to different product ratios in the electrolyte obtained by applying different voltages at the plasma electrode.

Figure 3: The first negative going scan of Pt CVs recorded in 0.01 M KOH at a scan rate of 50 mV s$^{-1}$ after aCGDE (550 V or 580 V for 30 s) at the PWE. The red and blue lines indicate that the AE is placed at 1.5 cm or 4.5 cm from the PWE, respectively. The CVs in a) were recorded immediately after aCGDE (step B1) and those in b) after holding the potential for additional 15 min at 1.00 V$_{\text{RHE}}$. The dashed and solid CVs were measured after applying 550 V or 580 V at the PWE, respectively.
S4: Influence of tubes around the plasma counter electrode

During aCGDE, H$_2$ is evolved at the plasma counter electrode. In order to prevent that the H$_2$ diffuses far into the electrolyte, where it could oxidize the auxiliary electrochemical Pt electrode, a glass tube was placed around the plasma counter electrode. In this way, the H$_2$ bubbles are directed outside the electrolyte (see Fig. 1 in the manuscript). Figure 4a shows CVs recorded at the Pt AE in 0.01 M KOH at a scan rate of 50 mV s$^{-1}$ directly after aCGDE (after step B1) and in Fig. 4b after aCGDE and additional 15 min waiting time (after steps B1 and B2). Corresponding measurements in a setup without glass tube are presented by the dashed curves. Overall the curves recorded with or without employing a glass tube look similar. Only when the AE is placed close to the PWE (1.5 cm) (red curves in Fig. 4a), the positive current density in the negative going scan in the potential region $> 0.60$ V$_{RHE}$ is larger when a glass tube was employed as if no glass tube was employed. As discussed in the manuscript, the positive current density was addressed to H$_2$O$_2$ oxidation. It appears as if the H$_2$ formed at the plasma counter electrode has an effect on the amount of H$_2$O$_2$ in the solution. The reason for this behavior remains, however, unknown.
Figure 4: The first negative going scan of Pt CVs recorded in 0.01 M KOH at a scan rate of 50 mV s$^{-1}$ after aCGDE (550 V for 30 s) at the PWE. The red and blue curves were obtained with Pt AEs placed at 1.5 cm and 4.5 cm from the PWE, respectively. The CVs were recorded a) directly after aCGDE and b) after waiting additional 15 min. In all cases, during the aCGDE and the subsequent waiting time, the potential of the AEs was kept at 1.00 V$_{\text{RHE}}$. The solid lines were recorded with a glass tube placed around the plasma counter electrode and the dashed lines without glass tube (see text for details).
S5: Influence of the upper potential limit on Pt surface oxidation

Fig. 5 shows the effect of applying higher upper potential limits (UPLs) on the CV of Pt recorded in 0.01 M KOH. The black solid line shows the CV with an UPL of 1.05 V_{RHE} and in green the CV after keeping the electrode at 1.0 V_{RHE} for 15 min (both in the manuscript with the same color code). Increasing the UPL to 1.25 V_{RHE} (black dashed curve), leads to an increase of the reduction peak at around 0.8 V_{RHE} in the negative going scan. The peak increases even more when the potential is kept at 1.20 V_{RHE} for 15 min (green dashed curve).

Figure 5: CVs of Pt electrodes recorded in 0.01 M KOH at a scan rate of 50 mV s^{-1}. The solid curve (black) shows the CV after cycling to an upper potential limit (UPL) of 1.05 V_{RHE} and the dashed black curves shows the CV after increasing the UPL to 1.25 V_{RHE}. The solid green curve was obtained by holding the potential at 1.0 V_{RHE} for 15 min and the dashed green curve after holding at 1.2 V_{RHE}.
S6: Temporal evolution of cyclic voltammograms after aCGDE

Fig. 6 shows the first and second cycles of the CVs recorded at a Pt AE directly after aCGDE (580 V for 30 s). For an AE placed at a distance of 4.5 cm from the PWE, in the first cycle (blue curve) a reduction peak is observed at around 0.6 $V_{RHE}$ in the negative going scan (see manuscript). In the second cycle (light blue curve) the reduction peak is smaller and the maximum is located at 0.8 $V_{RHE}$, hence at a similar potential than what is observed in a CV recorded before the experiment (black curve). The current densities related to ORR (additional negative current density) also decreased significantly in the second scan. Placing the electrode at 1.5 cm from the PWE, a large positive current density is observed in the first negative going scan at potentials $> 0.65 V_{RHE}$ (red curve). In the second cycle, the positive current density associated with the hydrogen peroxide reduction is much lower, but still measurable. Overall the CV is slightly shifted to more negative current densities for potentials $< 0.65$ V compared to the CV recorded before the experiment (black curve), which can be explained by the reduction of $O_2$ and $H_2O_2$ at the Pt electrode. In the first cycle (red curve), the CV is not as much shifted to lower current densities than in the second cycle (pink curve). This might be caused by an initially large $H_2$ concentration in the solution, which reacts with the Pt electrode giving rise to a positive current density which overlaps with negative current densities for ORR and HP RR. More importantly, a positive current density is still apparent at potentials $> .95 V_{RHE}$. This indicates that $H_2O_2$ is still present in the solution, which is oxidized at these potentials. The concentration is, however, much lower compared to the first cycle.

Continuous cycling reveals, that when the Pt electrode is placed at a distance of 1.5 cm from the PWE, it takes ca. 5 min until the CV looks almost identical to that recorded before the experiment, whereas when the electrode is placed at a distance of 4.5 cm from the PWE, it only takes ca. 3 min.
Figure 6: CVs recorded at a Pt AE in 0.01 M KOH with a scan rate of 50 mV s\(^{-1}\). The CV recorded before performing aCGDE (580 V for 30 s) is shown in black. The first two cycles recorded directly after aCGDE of an electrode placed at a distance of (i) 1.5 cm from the PWE are shown in red (1st Cycle) and pink (2nd Cycle) or (ii) of 4.5 cm from the PWE in blue (1st Cycle) and light blue (2nd Cycle). The inset shows a magnification of the potential range from 0.85 V\(_{\text{RHE}}\) to 1.10 V\(_{\text{RHE}}\).