Supporting Information

Continuous-Flow Electrochemical Production of H_2O_2 in a Gas Diffusion Electrode Microreactor

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S1. Design of the Experimental Setup, Catalyst Ink and Electrode Preparation

S1.1. Catalyst ink and electrode preparation

For electrochemical measurements, the catalyst ink was prepared as follows. A suspension with a concentration of 0.385 mg mL^{-1} was obtained by mixing 3.5 mg of KJB EC-300J powder (IMPAG AG, Switzerland) with 7.27 mL ultrapure water (18.2 MΩ cm, Milli-Q system), 1.80 mL 2-propanol (IPA; electronic grade, 99.999% trace metal basis, Sigma-Aldrich), and 18.36 µL perfluorosulfonic acid (PFSA) ionomer dispersion (Nafion^{TM} 117, 5 wt% in a mixture of lower aliphatic alcohols and water, Sigma-Aldrich). The mixture was homogenized in a sonication bath for 1 h.

Carbon paper (Sigracet 22 BB, Fuel Cell Store) was cut to size and dried in an oven at 115°C for 15 min to remove residual moisture, which could affect catalyst loading calculations. The electrodes were weighed before and after spray coating to determine the deposited mass. After sonication, 3 mL of the catalyst ink was spray-coated onto the carbon paper using an airbrush (Ultra, Harder & Steenbeck, nozzle 0.45 mm, Germany). During coating, the carbon paper was heated to 100°C to ensure complete drying of each layer. The coating was applied in two batches: first, 1 mL was deposited and dried in an oven at 115°C for 15 min, followed by deposition of the remaining 2 mL and a second drying step under the same conditions and cooled in a desiccator for 10 min. The final catalyst loading was determined to be 317 ± 64 µg cm^{-2} (mean ± SD, n = 6).

S1.2. Design of the experimental setup

The electrochemical microreactor housing was fabricated by CNC milling from PTFE blocks. In the anode compartment, a glassy carbon (GC) electrode was embedded as the counter electrode. The cathode compartment was equipped with a gas inlet and an integrated gas flow channel to accommodate the gas diffusion electrode (GDE). PTFE microchannel layers were inserted between the two half-cells, defining a channel thickness of 600 µm between the counter and working electrodes. Each half-cell has dimensions of 65 × 65 × 13.5 mm. The complete electrochemical reactor is formed by assembling two half-cells, resulting in overall dimensions of 65 × 65 × 27 mm, excluding additional sealing layers or external fittings. The electrolyte (0.1 M KOH, KOH hydrate, 99.995% Suprapur, Supelco, Merck KGaA) was delivered through the microreactor using a laboratory syringe pump (AL-4000 Programmable Double Syringe Pump, World Precision Instruments). Oxygen flow was controlled using a mass flow controller (Bronkhorst) and maintained at 7.0 – 8.3 sccm for all electrochemical measurements.

Immediately downstream of the microreactor, an in-line bubble remover (ElveFlow) was installed to eliminate bubbles generated during electrochemical measurements and to ensure uninterrupted electrolyte flow to the in-line sensor.

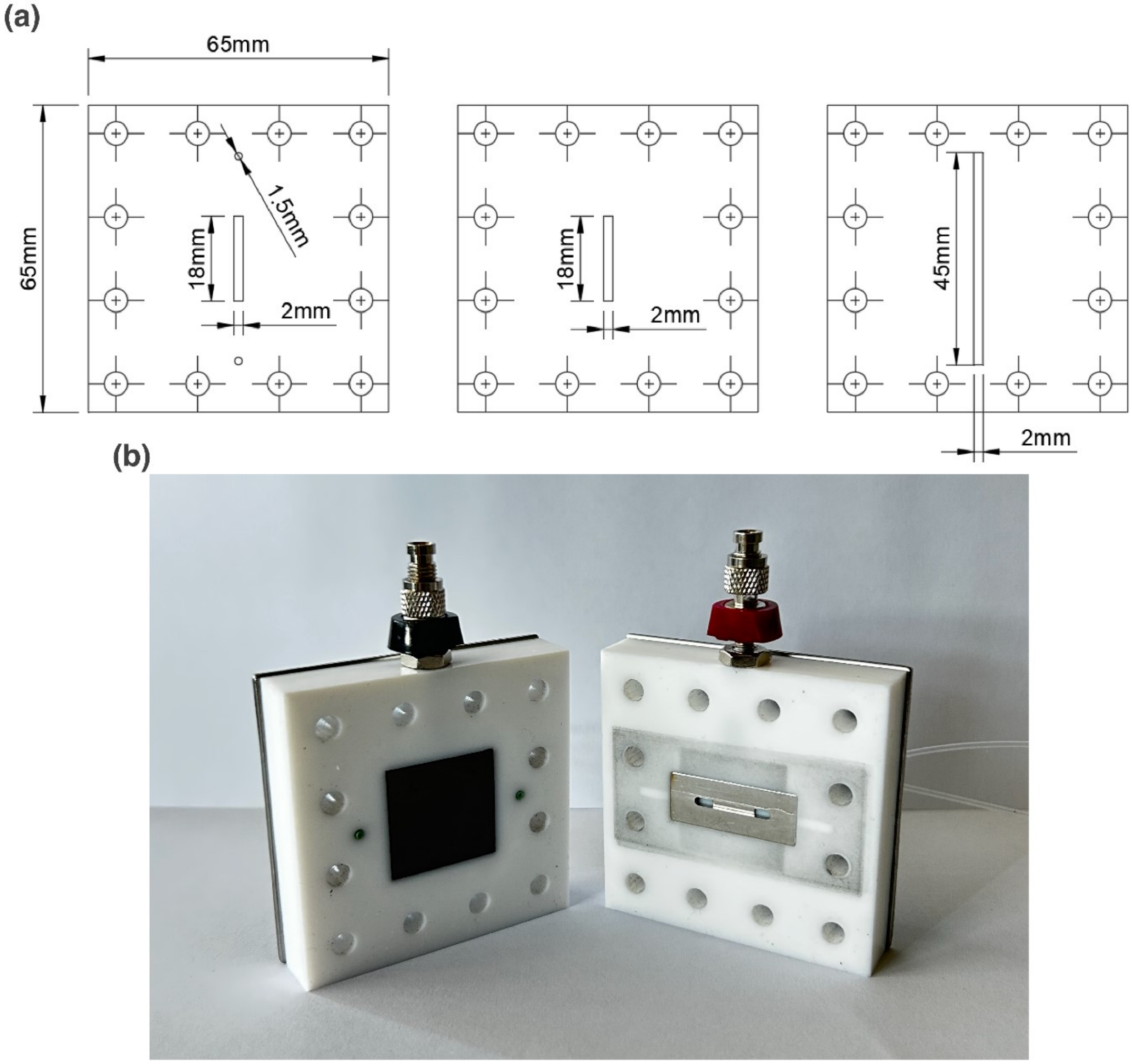

Fig. S1 (a) PTFE sheets determining the microchannel dimensions. **(b)** Housing of the electrochemical microreactor.

S2. Calibration of In-line Optical and Off-line Electrochemical Sensors

S2.1. In-line optical sensor

Optical sensor foils were prepared from liquid sensor formulations. Oxygen (O_2) sensor formulations contained 2 wt.% platinum(II)-6,13,20,27-tetrakis(4-fluorophenyl)tetrabenzoporphyrin (PtTPTBPF) or palladium(II)-6,13,20,27-tetrakis(4-fluorophenyl)tetrabenzoporphyrin (PdTPTBPF) as indicator dyes. The luminophores were immobilized on poly(styrene-co-divinilbenzene) microspheres (PS/DVB, 8 μm mean particle size, Sigma-Aldrich) dispersed in 7 wt.% hydrogel (Hydromed D7, AdvanSource Biomaterials) prepared in EtOH/H_2O (9:1, v/v).

For H_2O_2 sensing, ruthenium(IV) oxide hydrate (RuO_2, Sigma-Aldrich) was added to the PdTPTBPF-based formulation at 20 mg mL^{-1} and homogenized before coating.

Sensor foils were fabricated by knife-coating the liquid formulation onto a poly(ethylene terephthalate) (PET, Mylan, Goodfellow) support using a 3 mm coating bar, resulting in a wet film thickness of approximately 75 μm. Films were dried under ambient conditions, cut to size, and mounted into flow cells using double-sided adhesive tape. The assemblies were sealed with pressure-sensitive adhesive film (ThermalSeal RTS, Excel Scientific, Inc., USA) and an additional PET cover layer.

To increase the sensitivity of H_2O_2 measurements, excess dissolved oxygen was removed from the electrolyte using an oxygen scavenger. The scavenger was a gas-permeable tube (ChipShop Silicone Tubing, ID 0.5 mm / OD 2.5 mm, Darwin Microfluidics) immersed in a 2 wt.% sodium sulfite solution (Na_2SO_3, $\geq$ 98.0%, Sigma-Aldrich) and positioned upstream of the H_2O_2 sensor.

Before measurements, sensors were calibrated using aqueous H_2O_2 standards (0.4 mM – 8 mM) under experimental conditions. The standard solutions were prepared using 30% commercial H_2O_2 solution (Honeywell, Fluka^{TM}, 30% H_2O_2 (w/w)). More information regarding in-line optical sensors can be found in[1].

S2.2. Off-line electrochemical sensor

At higher applied currents, optical quantification of H_2O_2 was not feasible due to degradation of the glassy carbon (GC) counter electrode, which interfered with reliable optical readout. Under these conditions, H_2O_2 concentrations were determined using an independent electrochemical sensor.

During operation, once steady-state conditions were reached, the effluent stream was sampled directly from the microreactor outlet for electrochemical analysis. Direct sampling was essential to minimize H_2O_2 decomposition before measurement.

Electrochemical measurements were performed using a Metrohm PGSTAT302N potentiostat connected to a custom-built stirrer cell. A commercially available screen-printed carbon electrode (DRP C110, Dropsens) was used, comprising a silver quasi-reference electrode (Ag), carbon working electrode, and a carbon counter electrode. The working electrode was modified by drop-casting two 2.5 μL aliquots of a 1:1 dispersion (ethanol:water medium) of flash graphene and MnO_2 (particle size < 1 μm, Sigma-Aldrich), each at 1 mg mL^{-1}, and allowing them to dry under ambient conditions.

Measurements were performed in continuously stirred 0.1 M KOH containing 0.1 M KNO_3 to enhance ionic strength, reduce noise, and improve reproducibility. The optimal working potential (0.15 V vs. Ag) was determined after evaluating potentials between – 0.1 and 0.3 V vs. Ag. The sensor exhibited a dynamic range of 1 – 1000 μM, with two linear ranges (1 – 100 μM and 200 – 1000 μM), a sensitivity of 0.244 μA μM^{-1} cm^{-2}, and a calculated detection limit of 0.238 μM.

Chronoamperometric measurements were conducted at 0.15 V vs. Ag. After baseline stabilization, H_2O_2 was added stepwise for calibration using standard solutions, prepared from 30% H_2O_2 (Sigma-Aldrich) and regularly standardized to ensure reliability, followed by analysis of reactor sampling. All sample measurements were replicated four times to ensure accuracy and reproducibility[2].

Results of calibration for both in-line optical and off-line electrochemical sensor are presented in **Fig. S2**.

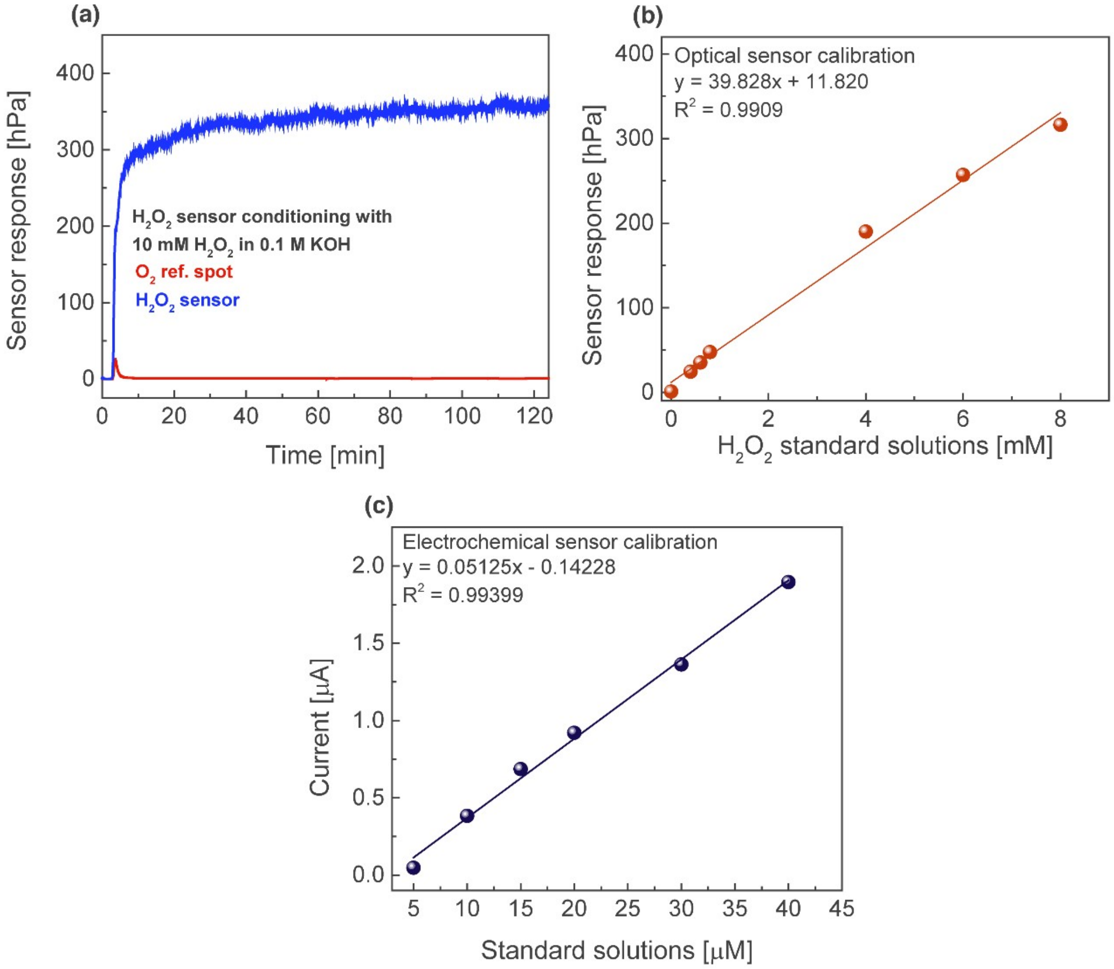

Fig. S2 (a) Conditioning of the optical sensor using a 10 mM H_2O_2 standard solution, required for accurate measurements. **(b)** In-line optical sensor calibration curve obtained prior to measurements. **(c)** Off-line electrochemical sensor calibration curve.

Table S1: In-line and off-line H_2O_2 concentrations produced at specific CP current:

Measurement series	Applied current during CP [mA]	In-line optical H_2O_2 concentrations [mM]	Off-line electrochemical H_2O_2 concentrations [mM]
1 (at E = 0.69 V vs. RHE from CV)	-0.5	2.6	N/A
2 (at E = 0.59 V vs. RHE from CV)	-0.75	3.3	N/A
3 (at E = 0.63 V vs. RHE from CV)	-1.0	4.0	N/A
4 (at E = 0.58 V vs. RHE from CV)	-1.5	8.0	N/A
5 (at E = 0.68 V vs. RHE from CV)	-2.4	N/A	12.0
6.1 (at E = 0.4 V vs. RHE from CV)	-4.15	N/A	21.6
6.2 (at E = 0.4 V vs. RHE from CV)	-4.45	N/A	23.6
6.3 (at E = 0.4 V vs. RHE from CV)	-3.8	N/A	22.6
6.4 (at E = 0.4 V vs. RHE from CV)	-4.07	N/A	21.6

S3. Characterization Techniques: Detailed Methodology

S3.1. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

Detailed information on the electrode composition and morphology was obtained using a high-resolution Thermos Scientific^{TM} Apreo 2^{TM} field-emission scanning electron microscope (FE-SEM). For plan-view imaging, the spray coated GDE was mounted on an adhesive conductive carbon tape (Agar Scientific) attached to an aluminum SEM stub. Cross-sectional imaging was performed by cutting the spray-coated electrode and mounting it perpendicularly on an aluminum stub using stainless steel support plates. SEM images were acquired at an accelerating voltage of 2 kV using an ETD side-mounted SE2 detector and a T1 segmented in-lens detector, with a working distance of 9.6 mm. Elemental analysis was performed by energy-dispersive X-ray spectroscopy (EDS) using ChemiSEM Technology at 15 kV and a beam current of 0.2 nA. A 60 mm^2 EDS detector was used for X-ray collection, and data were processed using the Aztec software package.

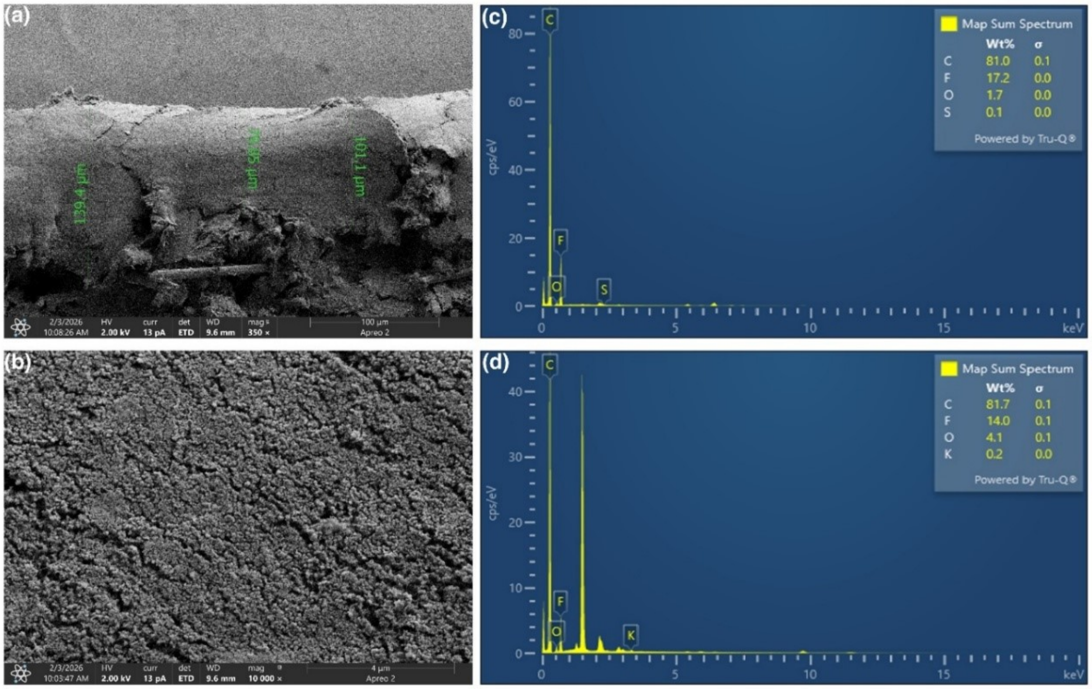

Fig. S3 (a) Cross-sectional SEM image showing thickness of the spray-coated catalyst layer between 139.4 µm and 79.85 µm. **(b)** Plan-view SEM image of the electrode surface after spray coating. **(c)** EDS spectrum of the GDE electrode before electrochemical measurements. **(d)** EDS spectrum of the GDE electrode after electrochemical measurements.

S3.2. Raman spectroscopy

Raman spectroscopy was performed using the Raman/AFM WITec Alpha 300 RAS with a 532 nm laser light with a power of 15 mW and 30 s integration time.

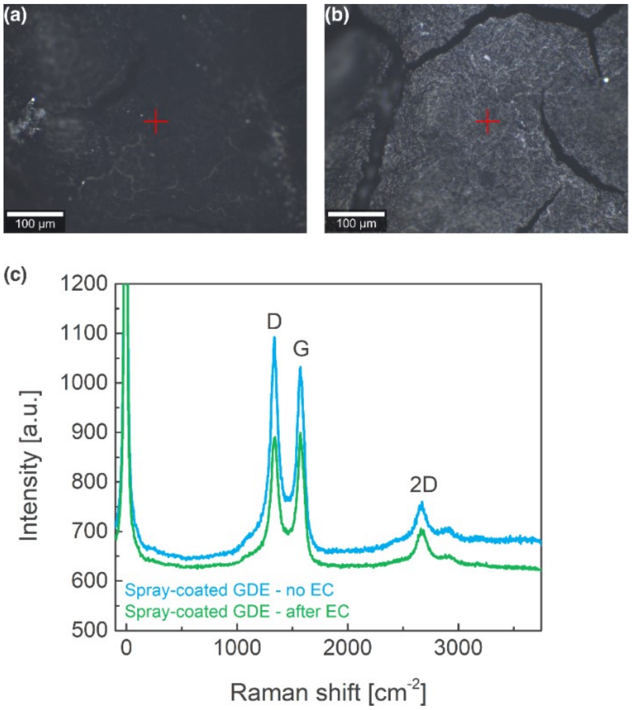

Fig. S4 (a) Raman map of the spray-coated GDE prior to electrochemical measurements. **(b)** Raman map of the spray-coated GDE after electrochemical operation (channel region). **(c)** Corresponding Raman spectra.

S3.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Versa Probe 3 AD (PHI, Chanhassen, USA) equipped with a monochromatic Al *Kα* X-ray source. The source operated at an accelerating voltage of 15 kV and an emission current of 13.3 mA. Powder samples were mounted on double-sided Scotch tape and positioned at the center of the XPS holder. Spectra were acquired for each sample over a 200 ×200 µm analysis area, with the charge neutralizer activated during data collection. Survey spectra were measured using a pass energy of 224 eV and a step size of 0.8 eV. High-resolution (HR) spectra were recorded with a pass energy of 27 eV and a step size of 0.1 eV. To ensure high-quality spectral data with a good signal-to-noise ratio, at least 10 sweeps were performed for each measurement. The energy scale of the XPS spectra and any possible charging effects were corrected by referencing the C=C peak in the C 1s spectrum of the carbon support, with a binding energy (BE) of 284.8 eV. Spectral deconvolution was carried out using MultiPak 9.9.1 and CasaXPS software. Shirley background correction was applied to all spectra. X-ray photoelectron spectroscopy (XPS) measurements were used to analyze the surface chemical composition of the samples before and after electrochemical measurements. For the C 1s region, the C–C/C=C component was fitted using an asymmetric LA line shape to account for the known asymmetry of graphitic carbon. For each core level, the full width at half maximum (FWHM) values were constrained to be the same for peaks assigned to the same chemical environment.

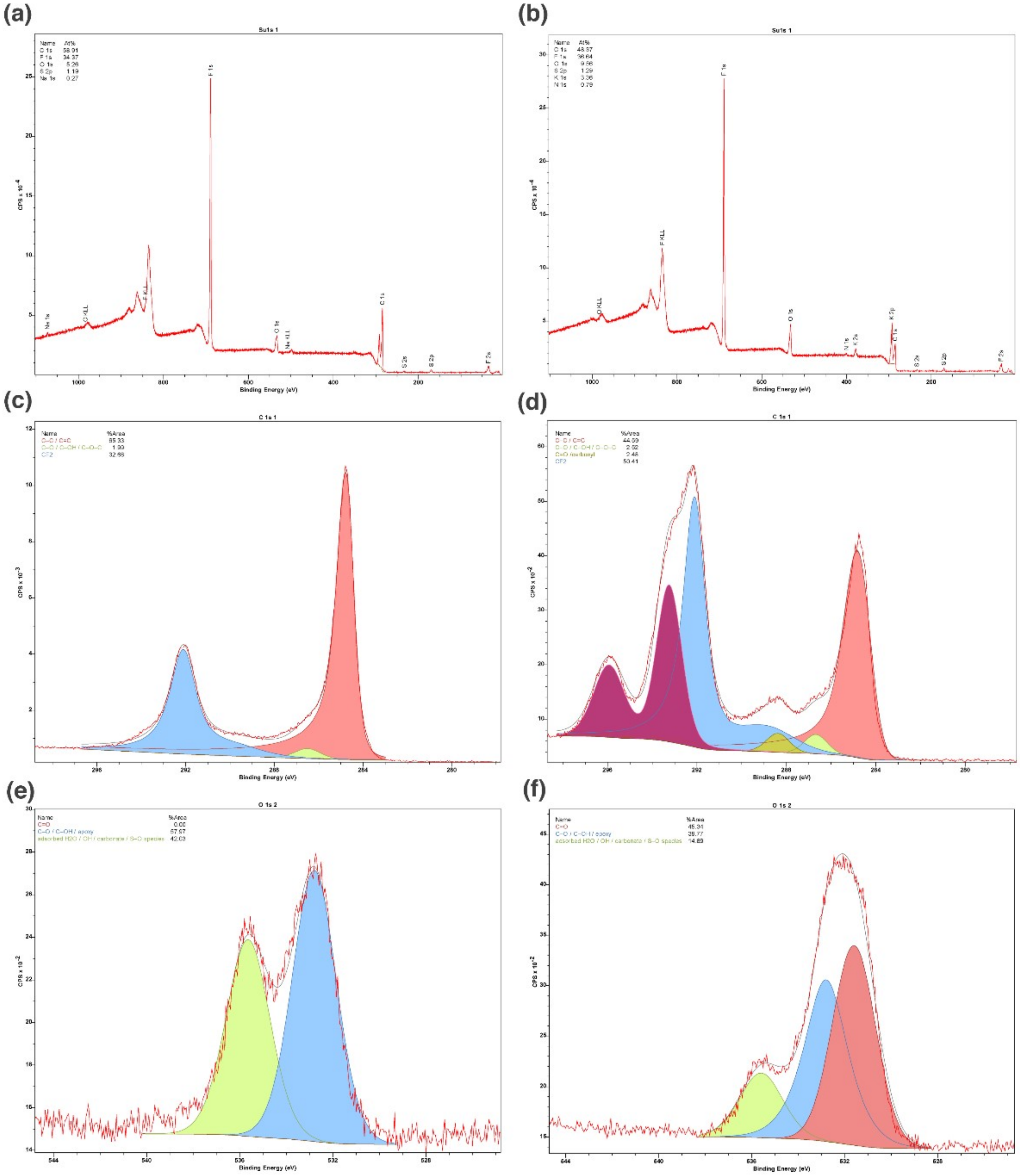

Fig. S5 (a) Survey spectra of spray-coated GDE before electrochemical measurements. **(b)** Survey spectra of spray-coated GDE after electrochemical operation. C 1s spectra of spray-coated GDE **(c)** before and **(d)** after electrochemical measurements. O 1s spectra of spray-coated GDE **(e)** before and **(f)** after electrochemical measurements

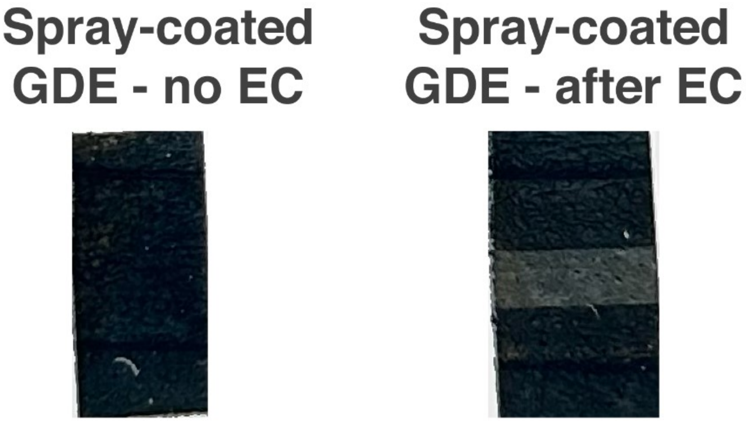

Fig. S6 Pictures of the spray-coated GDEs before (left) and after (right) electrochemical measurements.

S4. Supporting Calculations

*S4.1. Retention time calculation (**Eq. S1**):*

$$\tau = \frac{V}{\emptyset}$$

where:

- V – channel volume (21.6 µL).
- $\emptyset = 50*10^{-6}$ L min^{-1} (flow rate).

*S4.1. H_2O_2 concentration from in-line optical sensing (**Eq. S2**):*

H_2O_2 concentrations were calculated from the optical sensor response using the calibration slope and intercept:

$$C_{H_2O_2} = \frac{Sensor\ response - Intecept}{Slope}$$

where the slope and intercept were obtained from the calibration.

*S4.2. Faradaic efficiency (**Eq. S3**):*

The Faradaic efficiency for the H_2O_2 production during chronopotentiometric (CP) working regime was calculated according to:

$$FE\ (\%) = \frac{n * \emptyset * F * C_{H_2O_2}}{i_{appl.}}$$

where:

- $n = 2$ (number of electrons transferred).
- $\emptyset = 50*10^{-6}$ L min^{-1} (flow rate).
- $F = 96485$ C mol^{-1} (Faraday constant).
- $C_{H_2O_2}$ - measured H_2O_2 concentration (mol L^{-1}).
- $i_{appl.}$ – applied current during chronopotentiometry (A).

*S4.3. Full cell potential (**Eq. S4**):*

The full-cell potential was calculated from the working and counter electrode potentials recorded during electrochemical measurements:

$$E_{cell} = E_{CE} - E_{WE}$$

*S4.4. Specific energy consumption (**Eq. S5**):*

The specific energy consumption[3] was calculated for experiments yielding high H_2O_2 concentrations using the following equation:

$$E_{kWh/kg} = \frac{E_{cell} * n * F}{FE * M * (3.6 * 10^6)}$$

where:

- E_{cell} - experimentally determined cell potential (E vs. RHE).
- $n = 2$ (electrons per H_2O_2 formed in the $2e^-$ ORR).
- $F = 96485$ C mol^{-1}.
- $M = 0.0340147$ kg mol^{-1} (molar mass of H_2O_2).
- $3.6*10^6$ – conversion factor from J to kWh.

S5. Extended Electrochemical Results

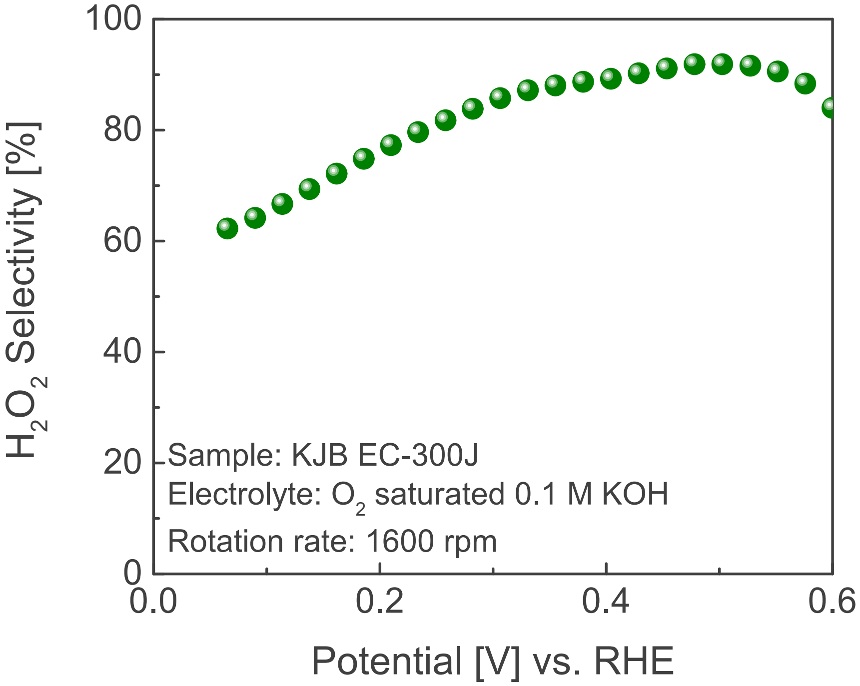

Fig. S7 H_2O_2 selectivity of the KJB EC-300J, determined by the rotating ring-disk electrode (RRDE) method.

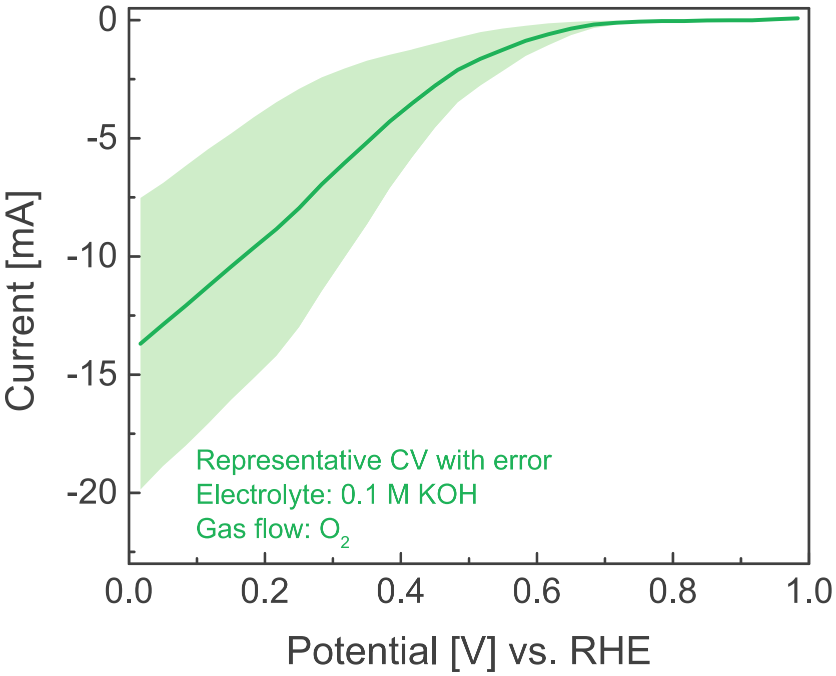

Fig. S8 Representative cyclic voltammogram (CV) of the microreactor equipped with a gas-diffusion (GDE) half-cell under operating conditions.

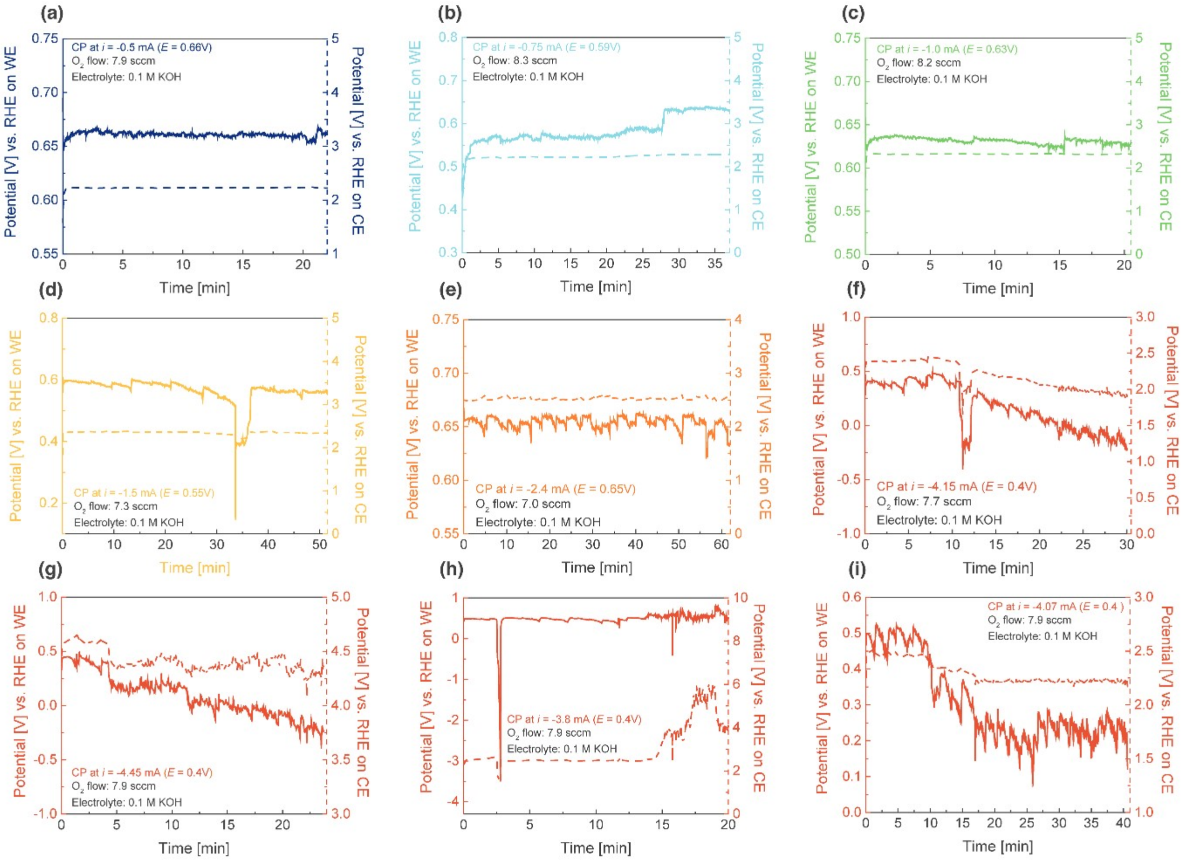

Fig. S9 (a) – (i) Chronopotentiometric (CP) data for H_2O_2 production in the GDE-equipped microreactor. The solid line represents the potential recorded at the working electrode, while the dashed line corresponds to the potential recorded at the counter electrode.

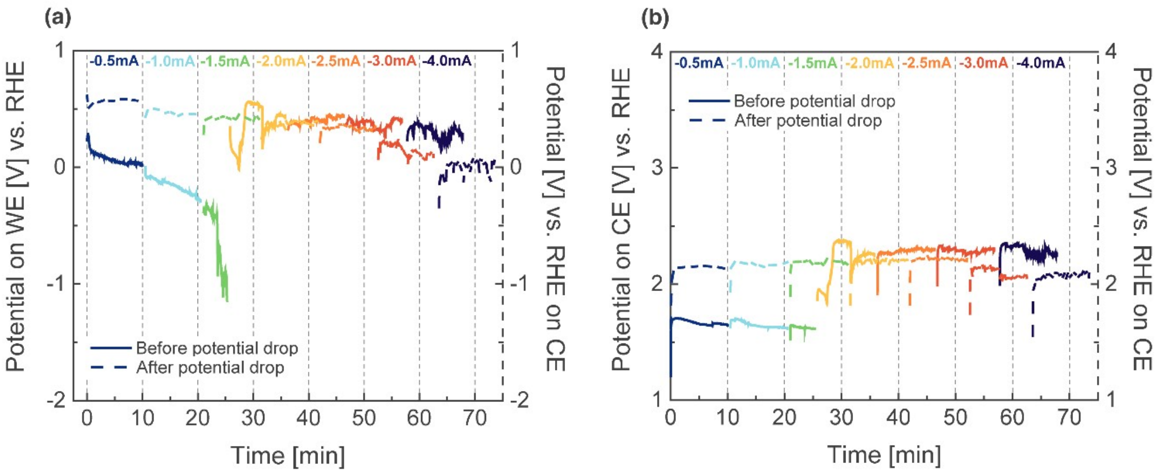

Fig. S10 (a) Chronopotentiometric (CP) response of the KJB EC-300J working electrode (WE) at different currents. Possible in situ activation during CP at -1.5 mA is indicated by the solid line, while subsequent repetitions with lower overpotentials are shown as dashed lines. **(b)** Corresponding potentials recorded at the glassy carbon counter electrode (CE).

Table S2. Electrode potentials and the specific energy consumption for H_2O_2 production with average concentration of 22.3 mM.

Repetitions (for the highest H_2O_2 conc.)	Potential on WE [V vs. RHE]	Potential on CE [V vs. RHE]	Faraday efficiency [%]	E_{cell} [V vs. RHE]	Specific energy consumption [kWh/kg]
6.1	0.08	2.05	83.7	1.98	3.72
6.2	-0.04	4.37	85.2	4.41	8.16
6.3	0.51	3.50	95.6	2.99	4.93
6.4	0.26	2.26	85.4	2.00	3.68

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