Supporting Information for:

**Operando** thin-layer ATR-FTIR spectroelectrochemical radial flow cell with tilt correction and borehole electrode

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This supporting information file contains additional images of the spectroelectrochemical cell as well as further experimental data supporting the claims formulated in the main text.

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1. SECM-type z-approach curves and tilt correction

![Figure S1. Negative feedback data of the WE/3ME ensemble approached to the IRE at t > 2500 s. It shows a deliberately induced tilt of the electrodes ME1, ME2 and ME3.](image)
The data in Figure S1 show deliberate tilting of the WE surface by successively lifting ME1, ME2 and ME3 by turning the corresponding micrometer screw. The data is discussed in the main text but it is pointed out here that despite the induced shift, the normalized tip currents at the beginning and at the end are essentially equal emphasizing the reproducibility to adjust a distinct geometry.

Figure S2. Calculation of the ME tip movements in a triangular geometry.

The 3D plot in Figure S2 shows the movement of the ME2 and ME3 tips along both, the z- and y-axis depending on a deliberate lifting of ME1. It shows that even ME2 and ME3 retract from its initial position along the z-axis though the change is not as severe as for ME1. The same holds for the y-axis which is indicative for a lateral movement. These calculations allow adjusting the WE/3ME plane in coplanar manner to the IRE surface plane.

2. Evaluation of the cell performance

Figure S3. IR spectra obtained during the chronoamperometric experiments shown in Figure 6 in the main text at 1.78 V vs. RHE in 1 mol L⁻¹ EtOH / 0.1 mol L⁻¹ KOH electrolyte after 9.5 min electrolysis time (solid lines) and first (dashed) as well as second (dotted) average spectrum after reducing the potential to 1.38 V vs. RHE.
3. EG oxidation at a Ni₄B-500-modified electrode

Figure S4: LSVs recorded at a dTL of 20 µm without a forced flux and with an applied flow rate of 5 µL min⁻¹ in 0.1 mol L⁻¹ KOH and in 1 mol L⁻¹ ethylene glycol / 0.1 mol L⁻¹ KOH, respectively, between 0.98 V vs. RHE and 1.78 V vs. RHE with a scan rate of 10 mV s⁻¹. The first LSVs is shown in a solid line, the second LSVs in dashed lines.

Figure S5. Comparison between conventional ≈ 4 mm and ≈ 8 mm (from ref. 5) GC disk electrodes with the BHE in 0.1 mol L⁻¹ KOH (solid) and in 1 mol L⁻¹ EG / 0.1 mol L⁻¹ KOH (dashed) from 0.98 V vs. RHE and 1.78 V vs. RHE with a scan rate of 10 mV s⁻¹. Before the measurements, the Ni₄B-500 electrocatalyst was conditioned in 0.1 mol L⁻¹ KOH by performing CVs between 0.98 V vs. RHE to 1.58 V vs. RHE with a scan rate of 100 mV s⁻¹. The measurements were performed in a conventional three electrode setup.

Figure S6: Same LSVs as shown in Figure S5 extended by measurements at a comparably large dTL of 3 mm.
Figure S7. Current densities obtained during a multistep amperometry experiment. The experimental procedure is summarized in the main text (cf. experimental part).

4. Reference spectra related to ethylene glycol oxidation

Figure S8. Normalized reference spectra related to EG oxidation.