Supporting information

Integration of Scanning Electrochemical Microscopy and Scanning Electrochemical Cell Microscopy in a Bifunctional Nanopipette Toward Simultaneous Mapping of Activity and Selectivity in Electrocatalysis

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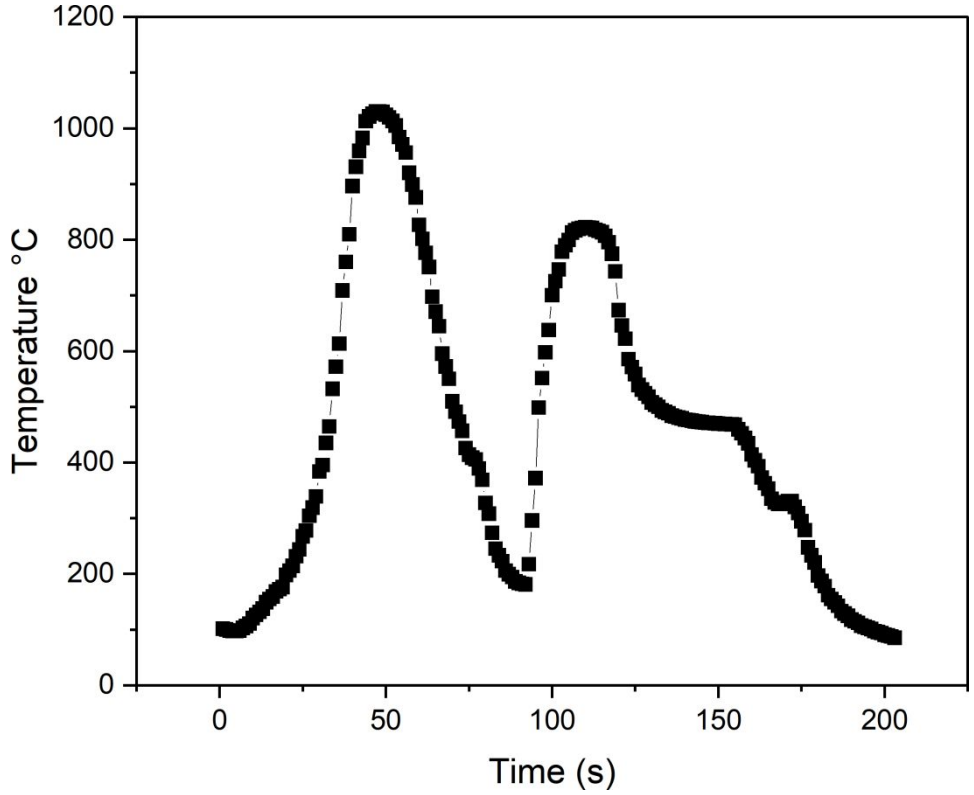

Figure S1. Temperature profile of the two-stage carbon pyrolysis. In the first stage from 0 to 100 s, pyrolytic carbon is deposited on the inner-wall of the pipette. In the second stage from 100 to 200 s, it extends in the entire heated volume of the pipette.

S2: Parameters used for the preparation of the SECCM dual probe:

For the FIB processing of the as prepared electrodes the used parameters are varying depending on the type of cut and on the size of the obtained probe. The initial FIB cut shown in Figure 2e is typically performed with the following parameters: 30 kV and 100-300 pA. The FIB milling step shown in Figure 2f is typically made with the following parameters: 30kV and 30 pA. The Pt deposition shown in Figure 2g is performed using the FIB with the following parameters: 30 kV and 10-30 pA. The deposition height is set as the size of the cut out done in the previous step plus 250 nm to create a slight "over" deposition of Pt/Ga. The consecutive FIB cuts for flattening and shaping the geometry of the dual-probe are made again with 30 kV and 30 pA.

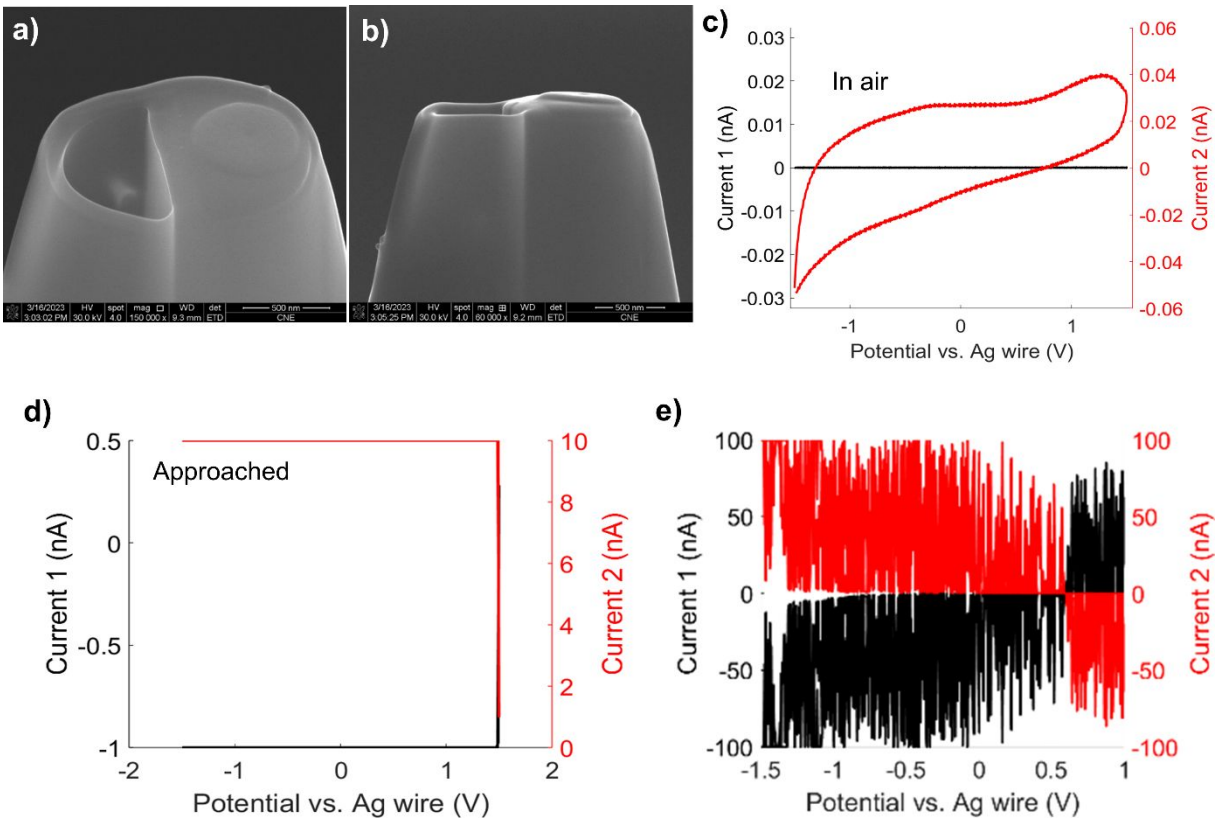

Figure S3. SEM micrograph of the end of a dual-probe (a, b) showing deposited Pt disk (right) and open barrel (left). The corresponding voltammetric responses in air (c) and after the overloaded approach (d). The noisy voltammetric responses are ascribed to a bad contact of the substrate and the droplet (e).

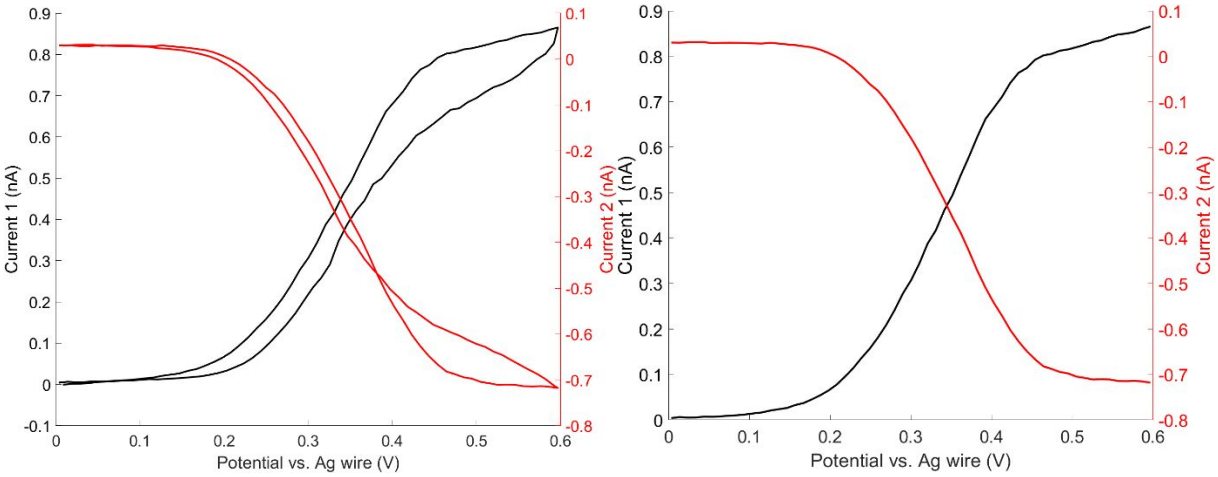

Figure S4. CV (left) and LSV responses (right) of the fabricated dual-SECCM/SECM probe when it is approached to an Au substrate surface (without back-retraction). The SECCM capillary is filled with 1 mM 1,1′-ferrocendimethanol in 0.05 M KOH.

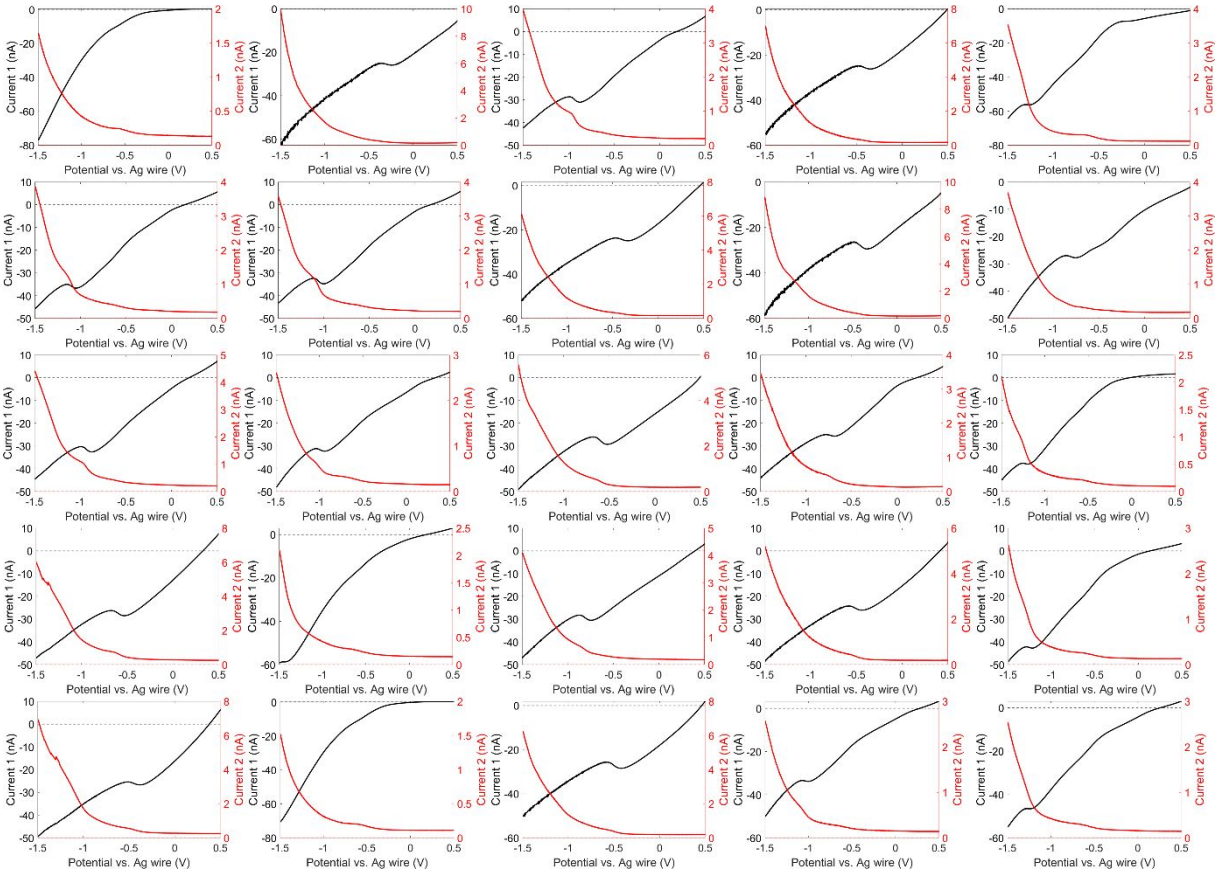

Figure S5. LSVs obtained in a 5 x 5 scan (25 spots) array measured with a semicircle-cut probe. Current 1 is the Au substrate current (black), and current 2 is the Pt-tip current (red). The SECCM capillary is filled with 0.05 M KOH.

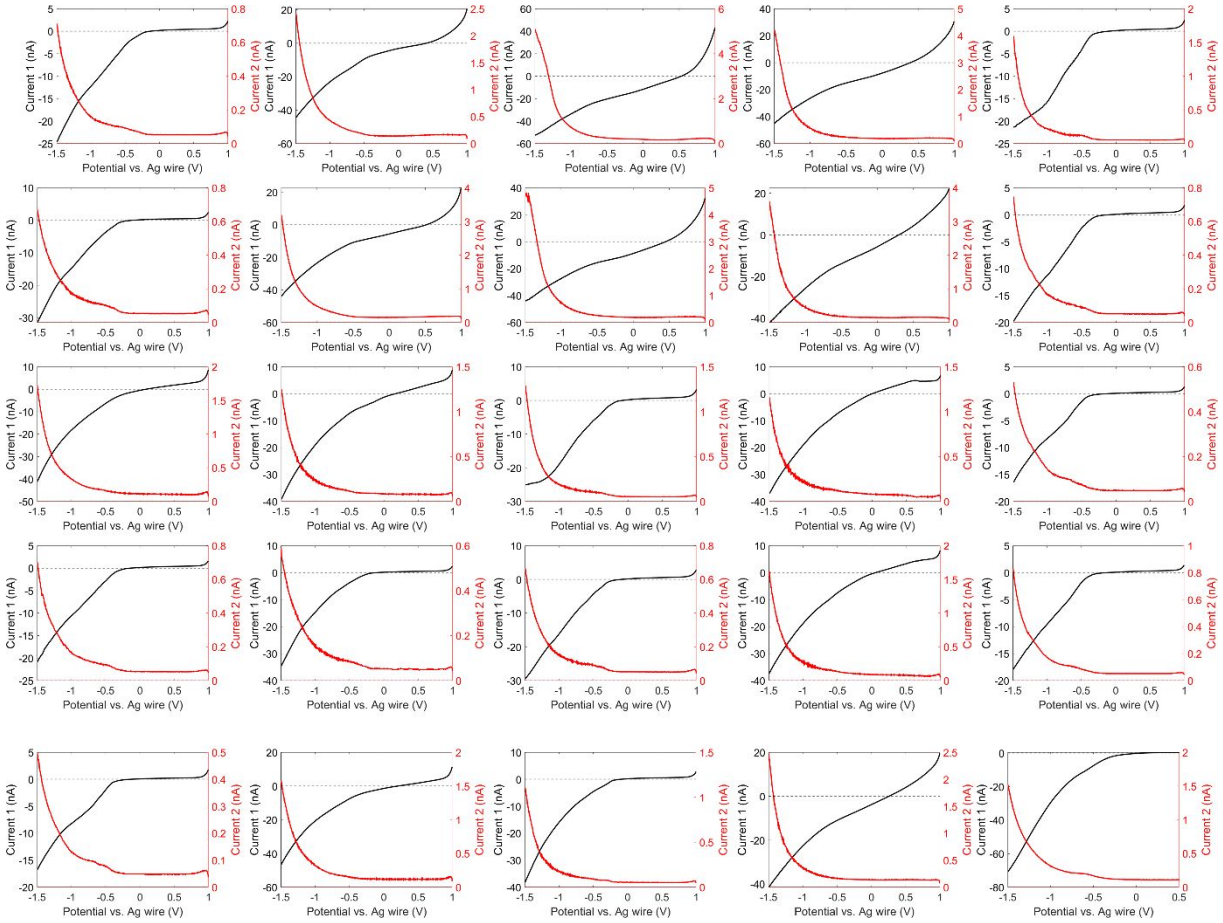

Figure S6. LSVs obtained in a 5 x 5 scan (25 spots) array measured with a different semicircle-cut probe. Current 1 is the Au substrate current (black), and current 2 is the Pt-tip current (red). The SECCM capillary is filled with 0.05 M KOH.

S7: Supporting Movie M1: Linear sweep voltammetry movie of the ORR current (current 1) at the Au substrate, constructed from a series of current maps in the potential range of 0 to -1 V. The SECCM capillary is filled with 0.05 M KOH.

S8: Supporting Movie M2: Linear sweep voltammetry movie of the H_2O_2 oxidation current (current 2) at the Pt tip, constructed from a series of current maps in the potential range of 0 to -1 V. The SECCM capillary is filled with 0.05 M KOH.