

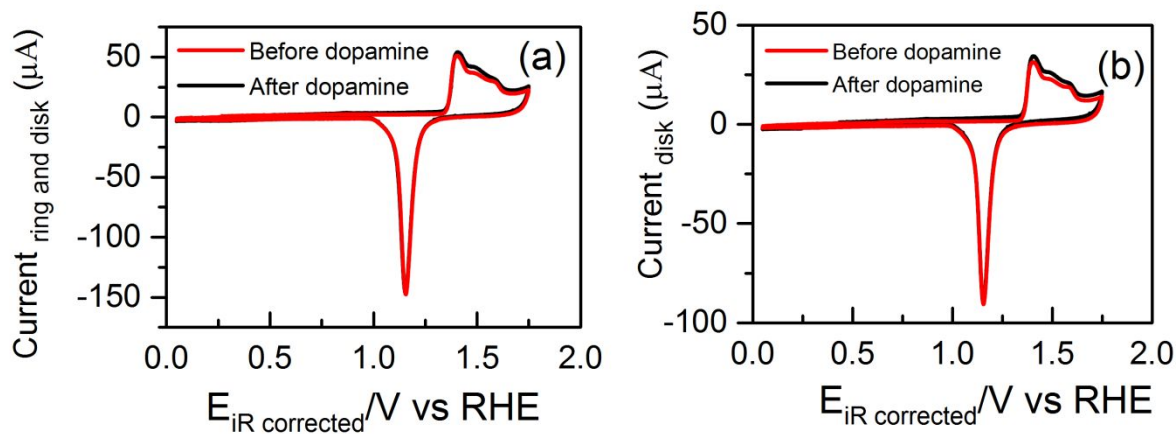
Supporting Information to

Competition between CO₂ reduction and hydrogen evolution on a gold electrode under well-defined mass transport conditions

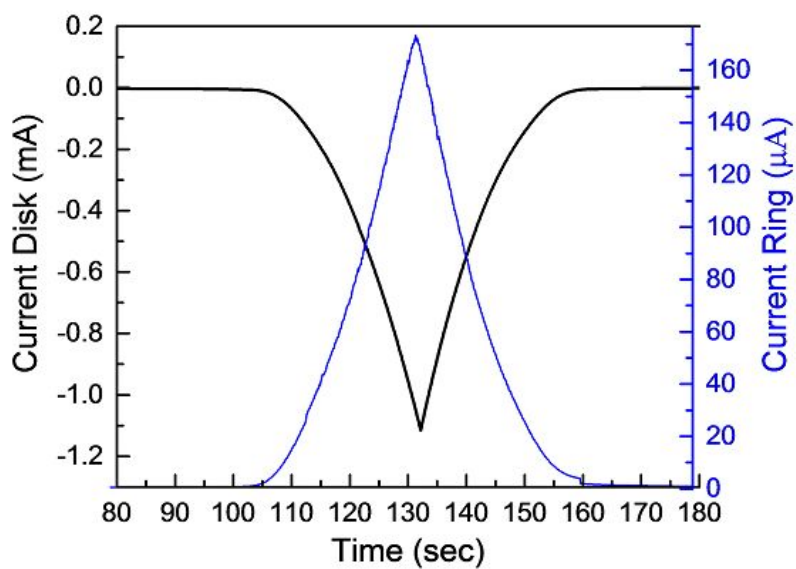
Akansha Goyal; Giulia Marcandalli; Vladislav A. Mints; Marc T.M. Koper*

Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

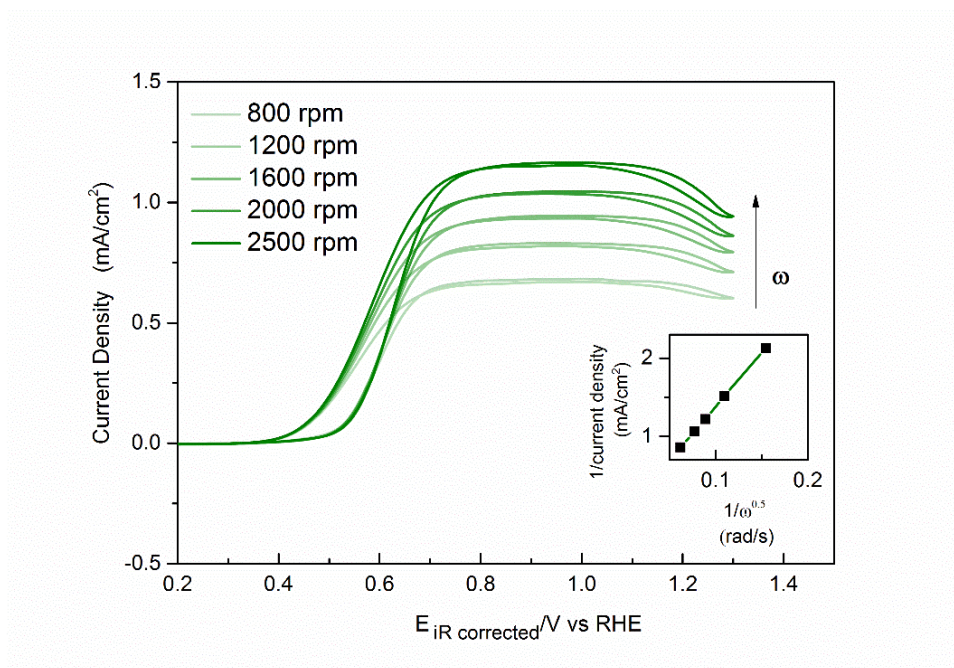
*email: m.koper@chem.leidenuniv.nl



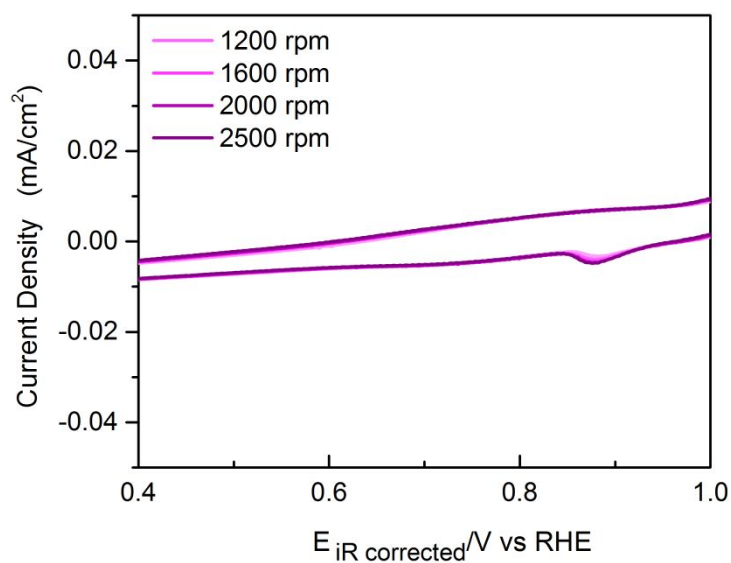
FigureS1 Characterization CV of (a) Ring and Disk and (b) Disk, in 0.1 M H₂SO₄, recorded at 50 mVs⁻¹. Red: before dopamine coating. Black: after dopamine coating.



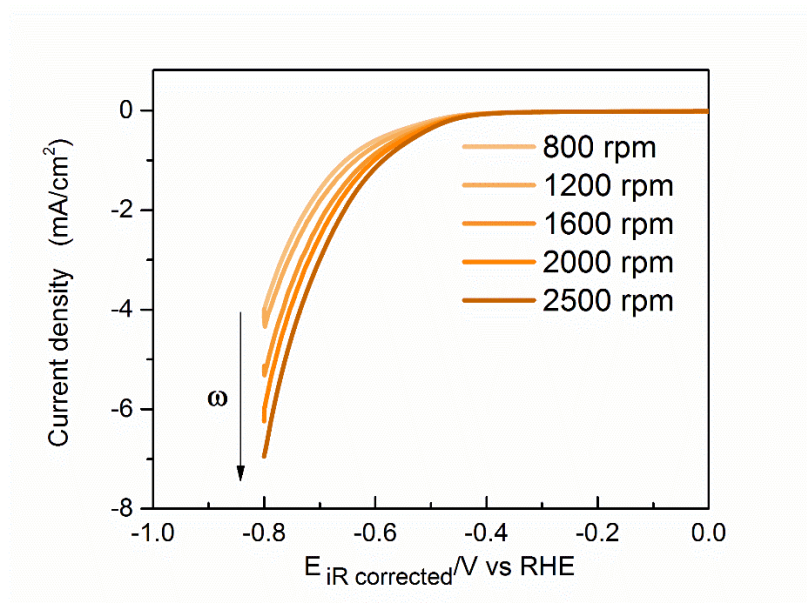
FigureS2 RRDE currents for the Au polycrystalline disk (black) and Au ring (blue) vs time, in CO_2 sat. 0.1 M NaHCO_3 (bulk $\text{pH} = 6.8$), recorded at 25 mVs^{-1} at 800 rpm .



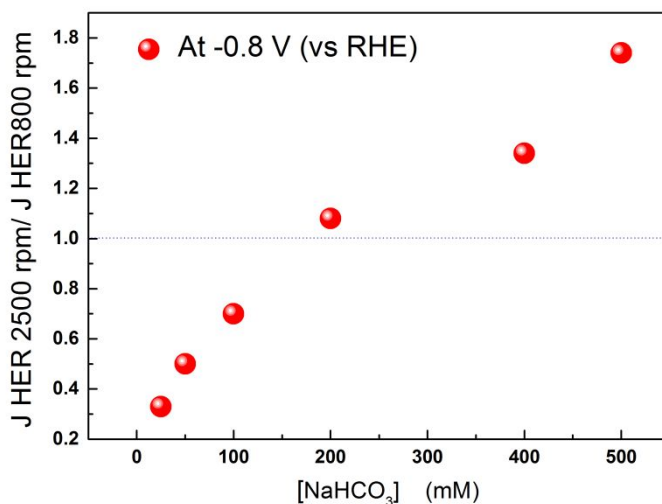
FigureS3 CO oxidation CV on Au polycrystalline surface at different rotation rates in CO sat. 0.1 M NaHCO_3 (bulk $\text{pH} = 9$), recorded at 25 mVs^{-1} from 0.2 V to 1.3 V vs RHE. The direction of the arrow indicates increasing rotation rate. Inset shows the Koutecky-Levich analysis for the CO oxidation currents at 1 V (vs RHE), where the calculated intercept of the line is 0.006 .



FigureS4 CV for Au polycrystalline surface in H_2 sat. 0.1 M NaHCO_3 (bulk $\text{pH} = 9$) in the potential window of CO oxidation recorded at 25 mVs^{-1} , at different rotation speeds.



FigureS5 CVs obtained for HER at different rotation rates using the RDE on Au polycrystalline surface in Ar sat. 0.5 M NaHCO_3 at 25 mVs^{-1} . The direction of the arrow indicates increasing rotation rate.



FigureS6 Ratio of HER current density at 2500 rpm and 800 rpm at -0.8 V (vs RHE) as a function of the sodium bicarbonate concentration in mM, obtained under Ar sat. conditions on Au polycrystalline surface using RDE. A ratio of less than 1 indicates that the water reduction is the dominant branch of HER and a ratio of greater than 1 indicates that bicarbonate mediated HER is the dominant branch.

Rotation speed (rpm)	Diffusion layer thickness (μm)	J limiting theoretical (mA/cm^2)
400	2.7	-36.6
800	1.9	-51.8
1200	1.6	-63.4
1600	1.4	-73.2
2000	1.3	-81.9
2500	1.1	-91.5

TableS1 Theoretically calculated diffusion limited currents for the two electron CO_2 reduction in the RDE set-up at different rotation rates, by using the Levich equation and Fick's first law of diffusion. Where diffusion coefficient of CO_2 is taken to be $1.6 \times 10^{-5} \text{ cm}^2/\text{s}$, the kinematic viscosity of water is taken to be $8.9 \times 10^{-3} \text{ cm}^2/\text{s}$, the Faraday's constant is taken to be 96500 C/mol , the number of electrons involved is taken to be 2 and the concentration of CO_2 in the bulk is taken to be 33 mM .¹⁻²

REFERENCES

1. Bard, A. J.; Faulkner, L. R., *Electrochemical methods : fundamentals and applications* Wiley: New York, **1980**.
 2. Ooka, H.; Figueiredo, M. C.; Koper, M. T. M., Competition between Hydrogen Evolution and Carbon Dioxide Reduction on Copper Electrodes in Mildly Acidic Media. *Langmuir* **2017**, *33* (37), 9307-9313.
-