

Electrochemical CO₂ Reduction

Product Distribution Screening on Cu-Co Thin Film Composition Spread Samples by Coupling of a Scanning Flow Cell to OLEMS



**Max-Planck-Institut
für Eisenforschung GmbH**

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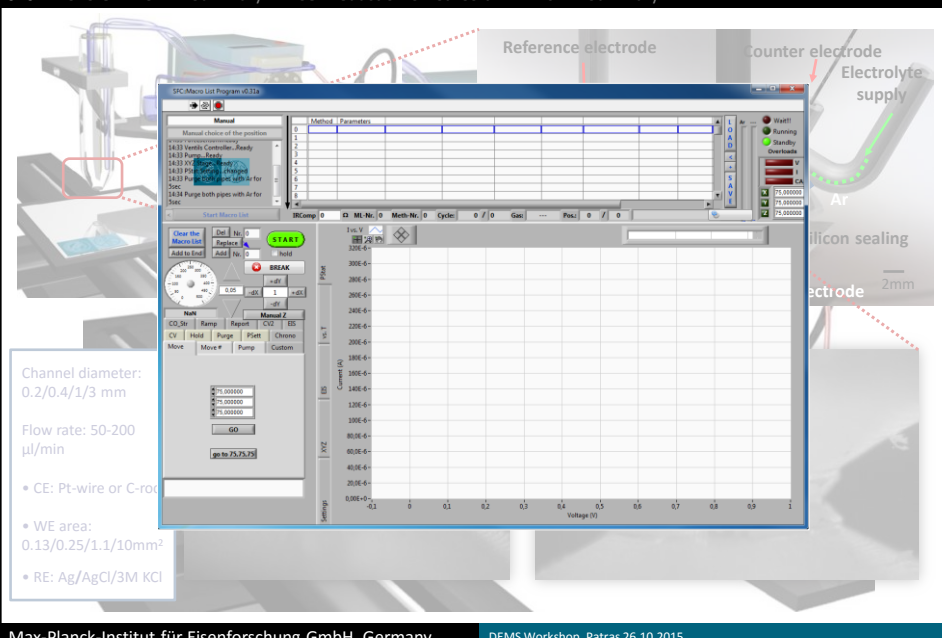
Jan-Philipp Grote, Aleksandar R. Zeradjanin, Serhiy Cherevko,
Karl J.J. Mayrhofer

E-mail: grote@mpie.de

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Scanning Flow Cell

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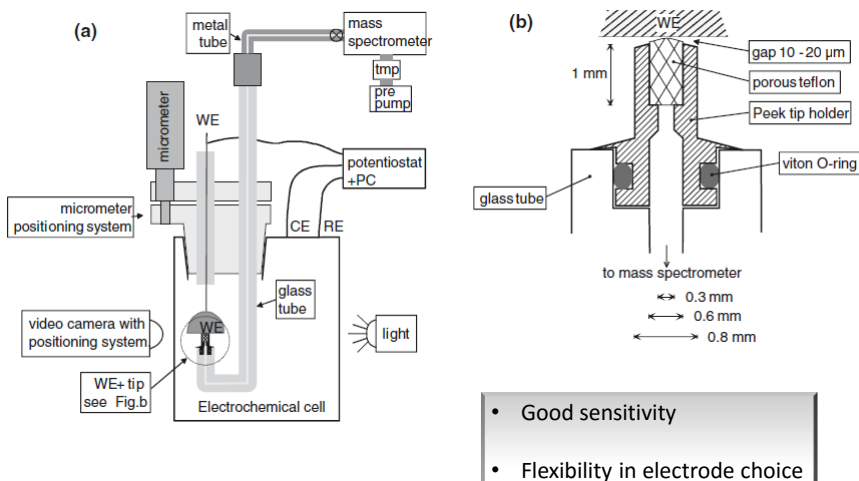


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Online Electrochemical Mass Spectrometer

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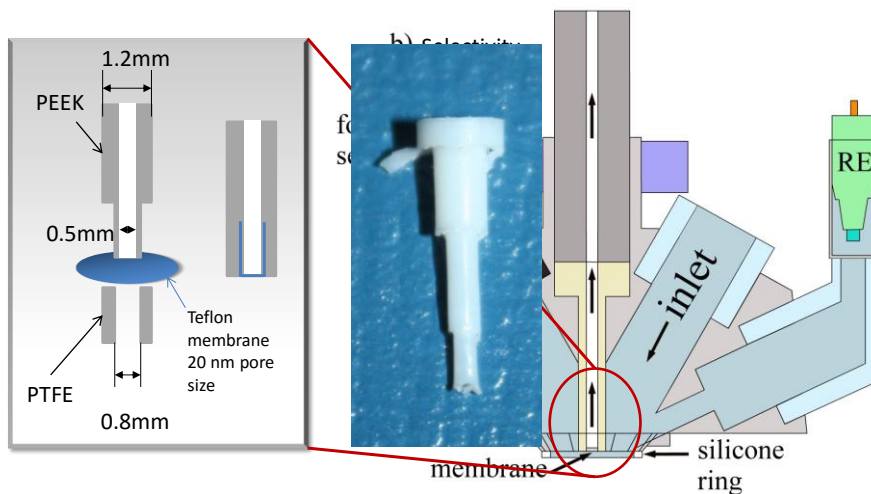
A. H. Wonders, T. H. M. Housmans, V. Rosca, and M. T. M. Koper, *J. Appl. Electrochem.*, **36**, 1215–1221 (2006)

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SFC-Online Electrochemical Mass Spectrometer

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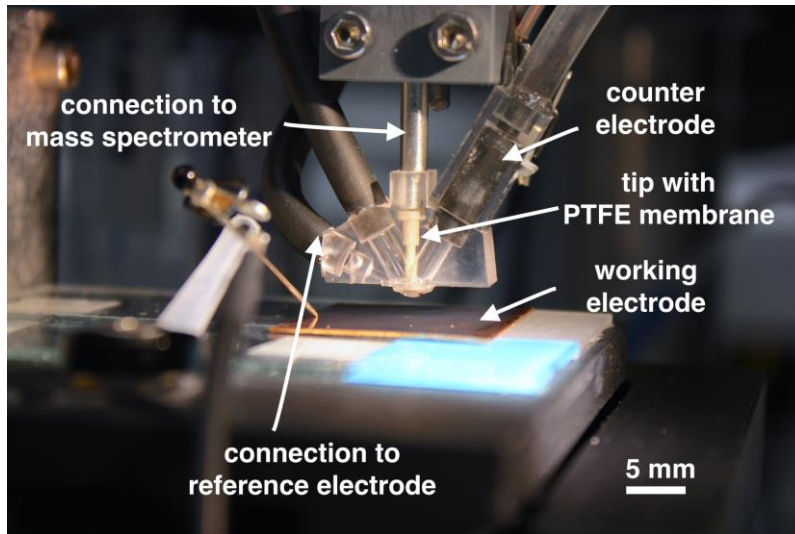
J.-P. Grote, A. R. Zeradjanin, S. Cherevko, and K. J. J. Mayrhofer, *Rev. Sci. Instrum.*, **85**, 104101 (2014)

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SFC-OLEMS

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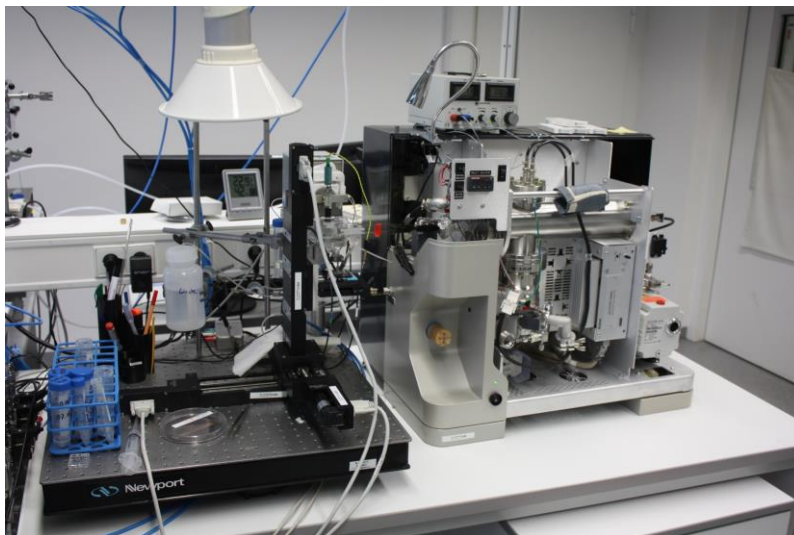


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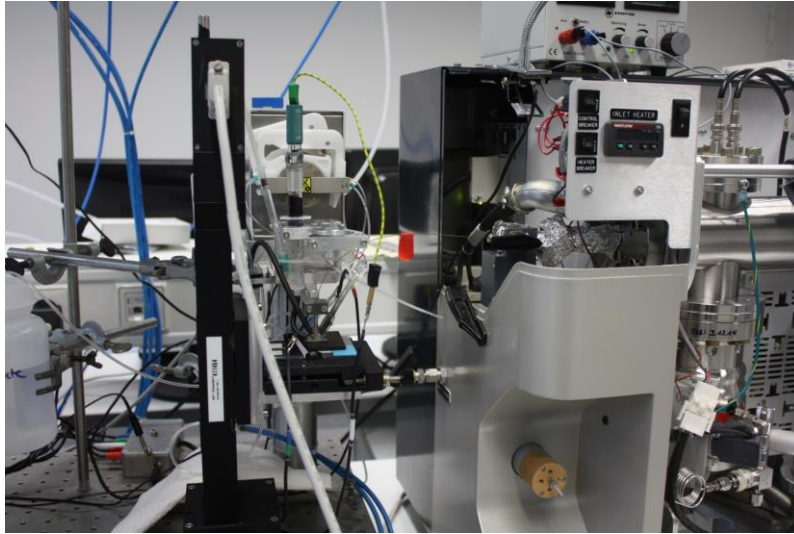


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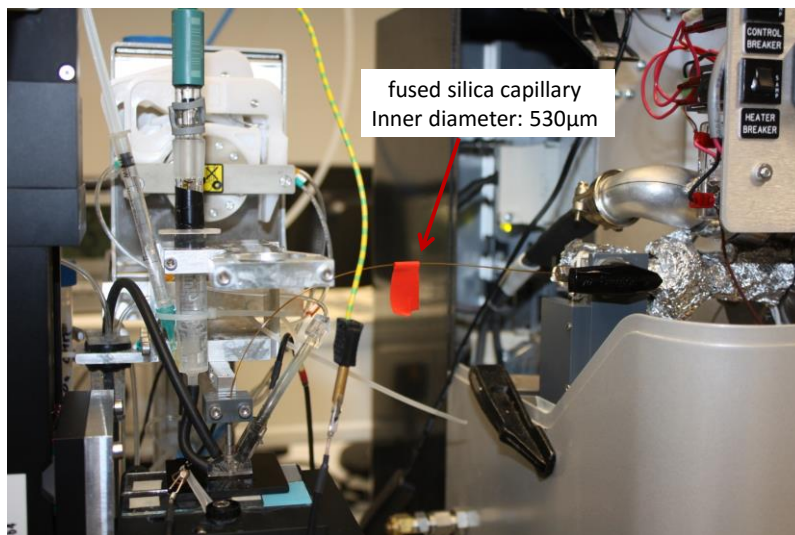


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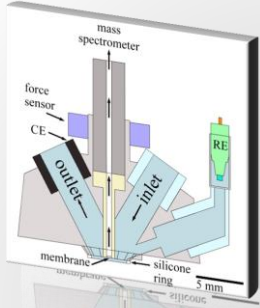
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Summary SFC-OLEMS

- Combination of product analysis ability of OLEMS with screening capability of SFC
- Flexibility in choice of electrodes: Bulk samples, thin films, high surface area catalysts
- Semi-quantitative results
- Sufficient response time ($\approx 2\text{-}3$ sec) and sensitivity
- Tested for CO₂ reduction, Mg corrosion, carbon corrosion and isotope labeled OER



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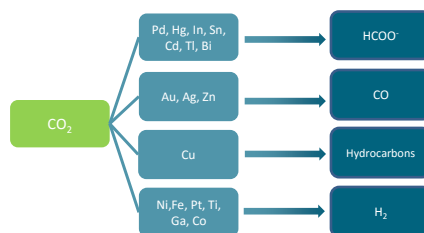
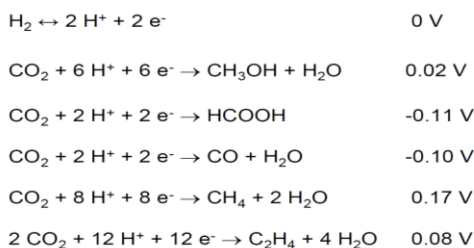
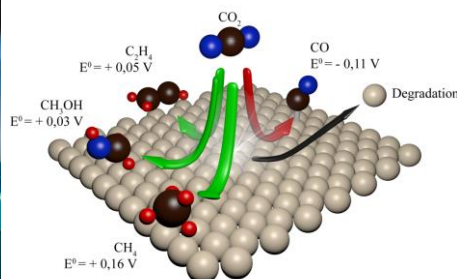
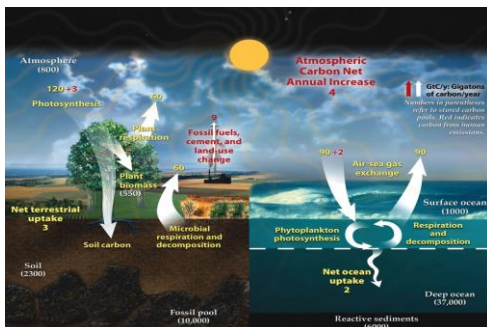
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CO₂ Reduction

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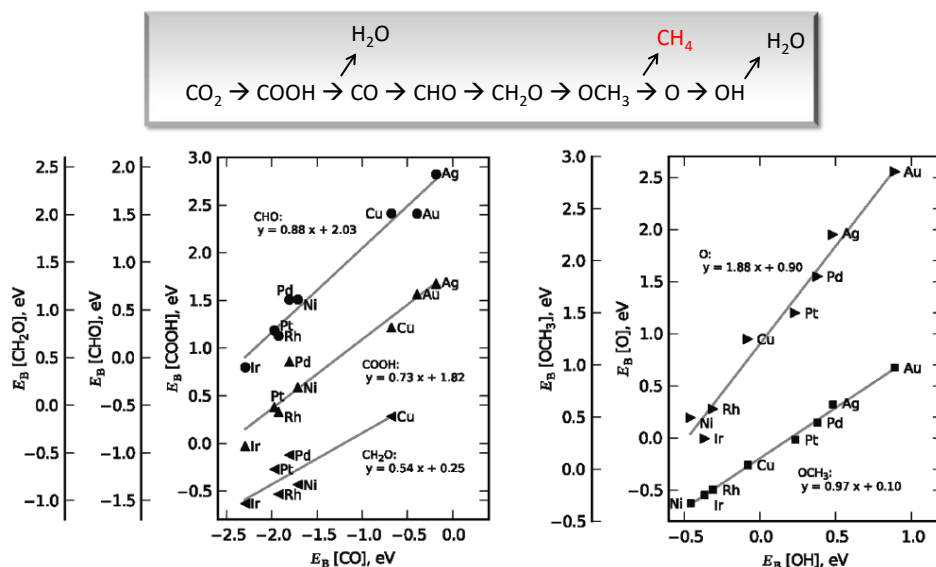
*Carbon cycle" by Diagram adapted from U.S. DOE, Biological and Environmental Research Information System. - <http://earthobservatory.nasa.gov/Features/CarbonCycle/>

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Scaling Relations

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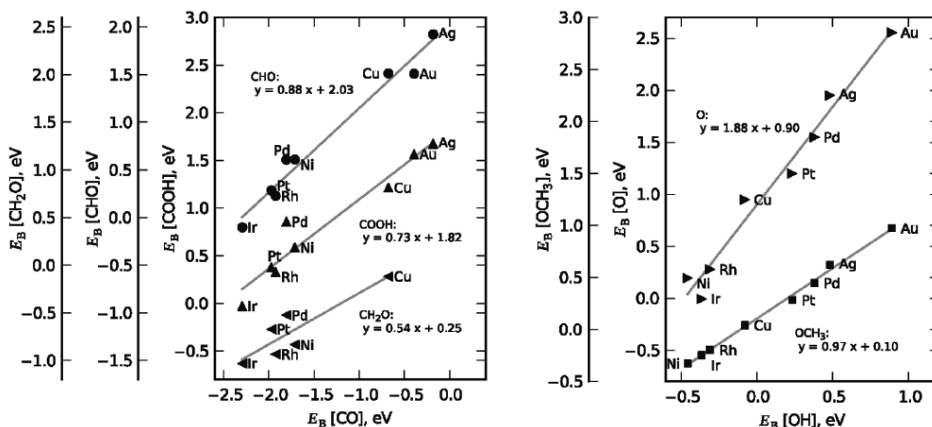
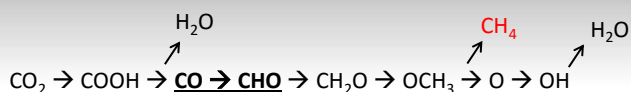
Peterson, A. A., & Nørskov, J. K. (2012). Activity Descriptors for CO₂ Electroreduction to Methane on Transition-Metal Catalysts. *The Journal of Physical Chemistry Letters*, 3(2), 251–258. doi:10.1021/jz201461p

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Scaling Relations

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Breaking Scaling Relations

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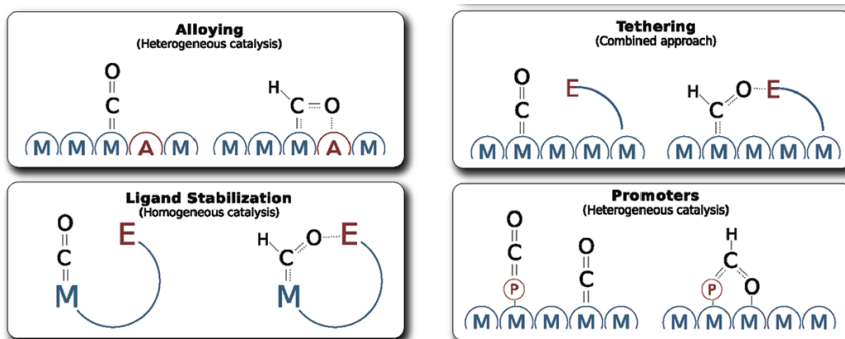


Figure 4. Suggested decoupling strategies exploiting the geometric differences between adsorbed CHO and adsorbed CO.

Peterson, A. A., & Nørskov, J. K. (2012). Activity Descriptors for CO₂ Electroreduction to Methane on Transition-Metal Catalysts. *The Journal of Physical Chemistry Letters*, 3(2), 251–258. doi:10.1021/jz201461p

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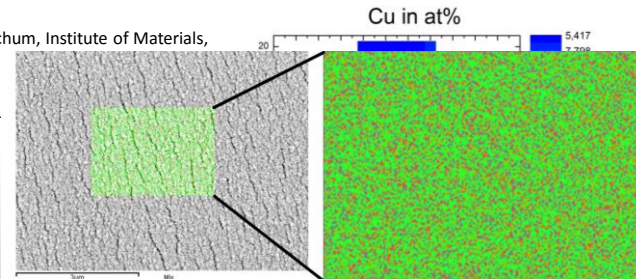
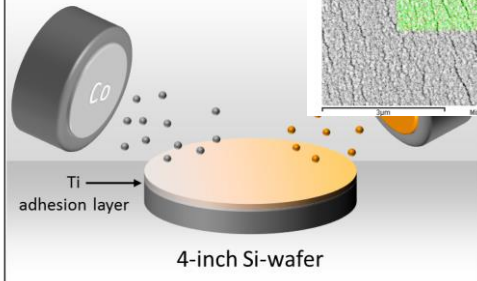
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SFC - Fast Screening of Alloys

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Prof. Ludwig, Ruhr-Universität Bochum, Institute of Materials,
RUB Faculty of Mechanical Engineering

Argon atmosphere



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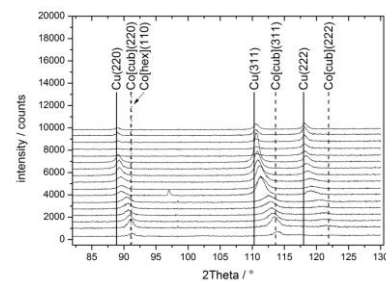
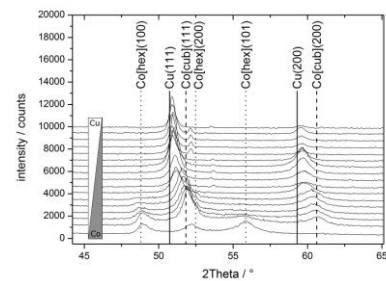
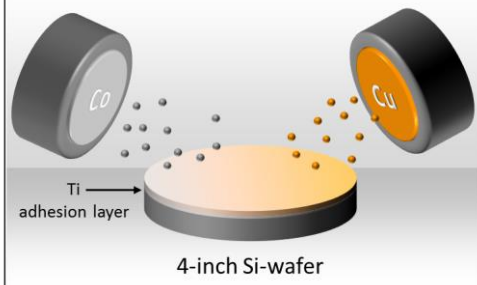
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SFC - Fast Screening of Alloys

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Prof. Ludwig, Ruhr-Universität Bochum, Institute of Materials,
RUB Faculty of Mechanical Engineering

Argon atmosphere



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Fragments



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Fragment Matrix												
Add Chemicals		Sensi tivity	Relative Abundance									
			m/z 2	m/z 14	m/z 15	m/z 18	m/z 26	m/z 28	m/z 31	m/z 32	m/z 40	m/z 44
<input checked="" type="checkbox"/>	H2	.175	100									
<input checked="" type="checkbox"/>	N2	1.000		4.98305178	0.01079979			100				
<input checked="" type="checkbox"/>	CH4	.698	0.5	15	81			0.09				
<input checked="" type="checkbox"/>	H2O	.800	0.12775634			100						
<input checked="" type="checkbox"/>	C2H4	1.000		2.14726949	0.78293705		49.52132034	100				
<input checked="" type="checkbox"/>	CO	1.000		1.22056949				100				
<input checked="" type="checkbox"/>	CH3OH	1.000	0.37529206	3.36012793	22.14814377			4.69622278	100	69.61496735		
<input checked="" type="checkbox"/>	O2	.980							0.19703659	100		
<input checked="" type="checkbox"/>	Ar	1.500									100	
<input checked="" type="checkbox"/>	CO2	1.860						4.80687332				100

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Fragments



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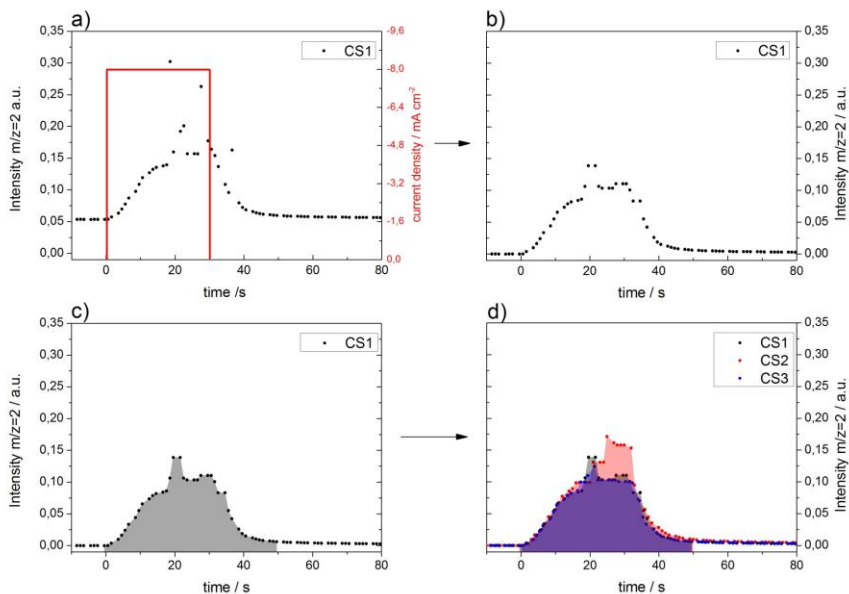
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<input checked="" type="checkbox"/>	O2	.980							0.19703659	100			
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<input checked="" type="checkbox"/>	CO2	1.860						4.80687332					100

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Measurement Procedure

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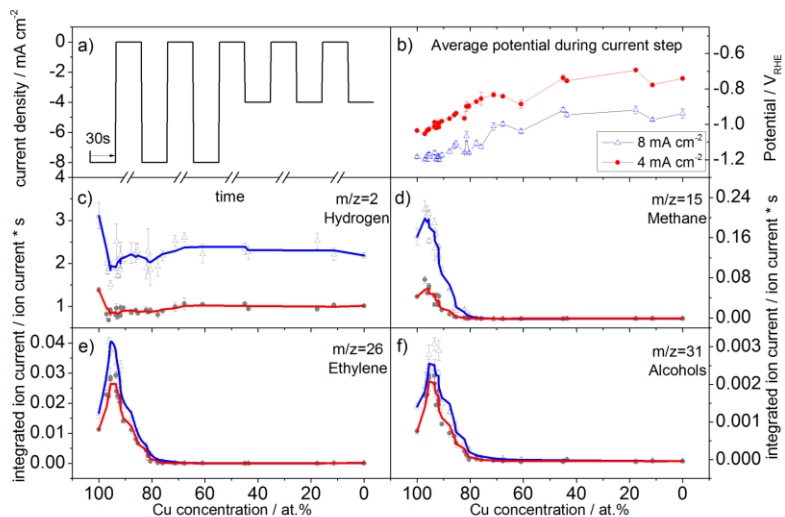


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Galvanostatic product distribution

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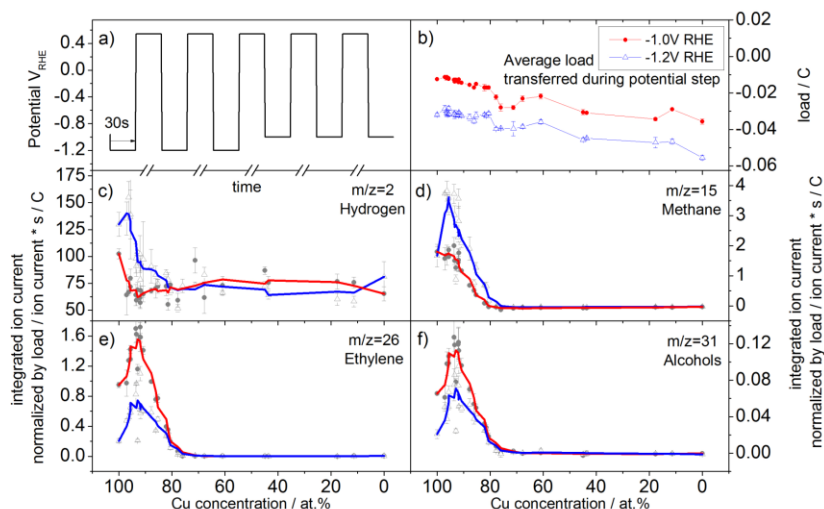


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Potentiostatic product distribution

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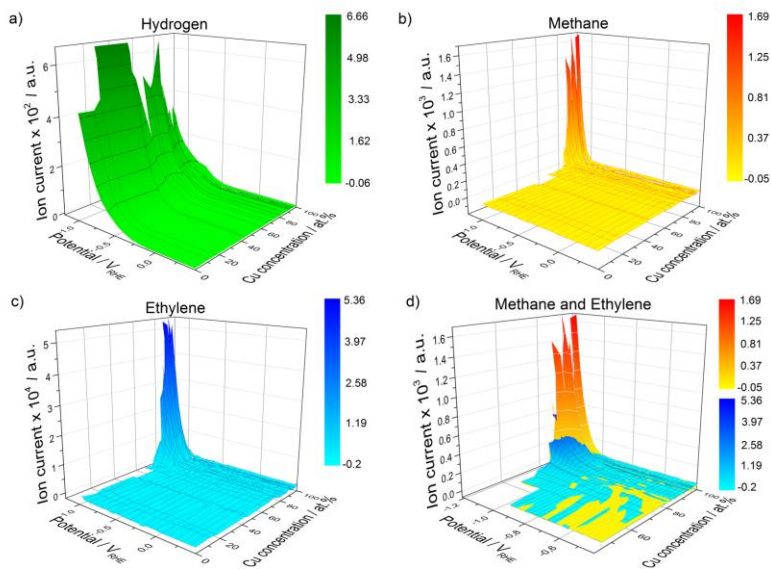


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Cyclic voltammetry

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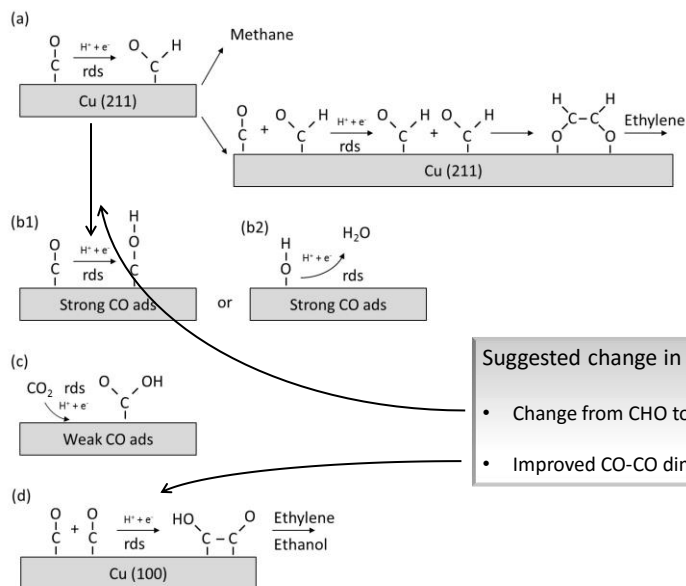


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Change in reaction mechanism?

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Suggested change in reaction mechanism:

- Change from CHO to COH intermediate
- Improved CO-CO dimer formation

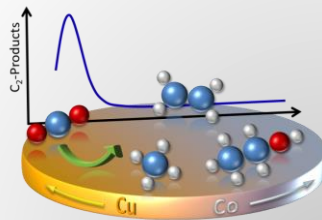
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Summary Cu-Co

- Mixing Cu with Co can shift selectivity towards C₂ products while overpotential is slightly reduced
- Change in intermediate product from CHO to COH or improved CO-CO dimer formation might lead to shift towards C₂ products
- Transfer of the results to nanostructured surfaces of GDE
- Influence of cobalt on pre oxidized and electrochemically reduced electrodes

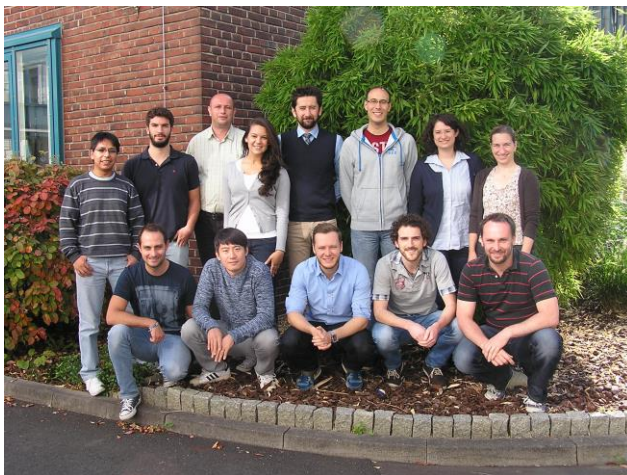


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Thanks for your attention!



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Electrocatalysis Group from Max-Planck-Institut für Eisenforschung

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