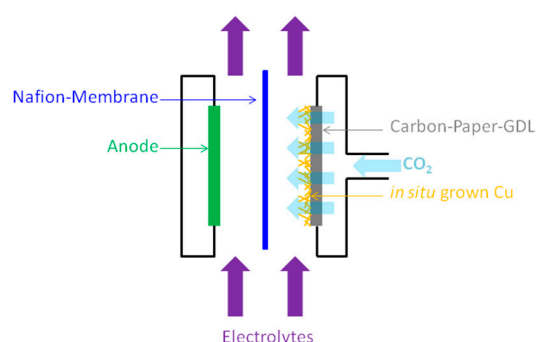


Supplementary Materials: Reactivity of Copper Electrodes toward Functional Groups and Small Molecules in the Context of CO₂ Electro-reductions

Bernhard Schmid, Christian Reller, Sebastian S. Neubauer, Maximilian Fleischer, Romano Dorta and Guenter Schmid

Feedstock vs. Heat value: a Comparison for Ethene:

The “deutsche Industriebank AG (IKB)”¹ listed ethene with 750 € (863 USD) (Feb 2015) per ton. The stock exchange price for natural gas (sole energy carrier) was 1.44 €/mmBTU (1.65 USD) at this time. The heat of combustion for ethene is 1411 kJ/mol. A ton of ethene has a total heat of combustion of 47.6 mmBtu. Thusly the value of ethene as natural gas like energy carrier was 68 € (78 USD) as opposed to 750 € (863 USD) as chemical feedstock in spring 2015. (Parity of 1€ = 1.15 USD used)



Scheme S1. Illustration of the applied flow cell concept.

Table S2. Summary of the reactivity screening on Cu-nano-dendrite bases catalyst.

| reactant | E_{WE} /V vs. Ag/AgCl | Q_{eq} /Fmol ⁻¹ | products except H ₂ | conv. / % | HER-suppression / % |
|--------------------------|-------------------------------|---------------------------------|-----------------------------------|--------------|------------------------|
| K(formate) | no change | 6.3 | none | none | none |
| K ₂ (oxalate) | no change | 4.1 | none | none | none |
| K(acetate) | no change | 6.3 | none | none | none |
| acetamide | no change | 4.1 | none | none | none |
| methane | no change | 0.042 | none | none | none |
| ethene | no change | 0.042 | ethane | 0.03 % | < 10 % |
| ethyne | -1.65 | 0.054 | ethene, ethane | 1.5 % | 61 % |
| ethanol | no change | 2.4 | none | none | none |
| ethylene glycol | no change | 2.3 | none | none | none |

| | | | | | |
|--------------------------------|-----------|-----|--|------------------|--------|
| allyl-alcohol | -1.67 | 4.4 | n-propanol | 34 % | 15 % |
| propargyl-alcohol | -1.41 | 3.7 | allyl-alcohol, n-propanol | full | > 95 % |
| acetaldehyde | -1.39 | 2.3 | ethanol | 25% [‡] | > 95 % |
| acetone | no change | 4.8 | <i>i</i> -propanol | 9% | < 10 % |
| glyoxal | -1.29 | 2.1 | ethylene glycol, glycolic acid * | full | > 95 % |
| K ₂ (fumarate) | -1.34 | 4.1 | succinate | full | > 95 % |
| 1,1-dimethoxy-ethane | no change | 4.4 | none | none | None |
| ethylene glycol vinyl ether | no change | 3.7 | ethene, ethane, glycol | 6 % | < 10 % |
| formaldehyde | -1.32 | 3.2 | methanol | full | > 95 % |
| 2-butyne-1-ol | -1.66 | 4.8 | crotyl alcohol | full | 91 % |
| vinyl acetate | -1.42 | 3.0 | acetate, ethanol, ethene | full | 83 % |

* The bulk of the glyoxal underwent benzilic-acid-rearrangement to glycolic acid ⁶³.

[‡] Calculated from the yield of ethanol – no account for reduced products of the competing aldol condensation.

Remark for the presentation of NMR-Spectra:

The NMR spectra as presented here were recorded in water containing 50 mM fumaric acid as internal reference. The residual water artifact shows at 4.79 ppm. The fumarate resonates at 6.49 ppm. These signals will remain unlabeled in the spectra.

Reduction of Allyl Alcohol:

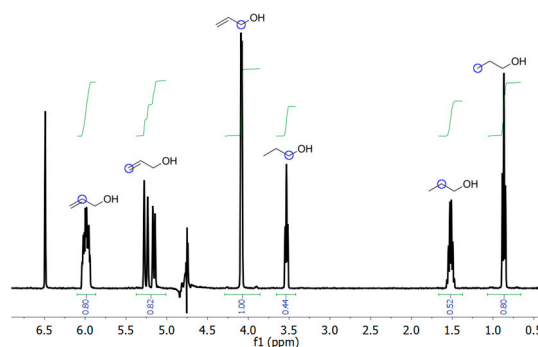


Figure S3: ¹H NMR spectrum of the electro reduction experiment with allyl-alcohol.

New resonances of *n*-propanol appeared. The allyl alcohol was only partially converted.

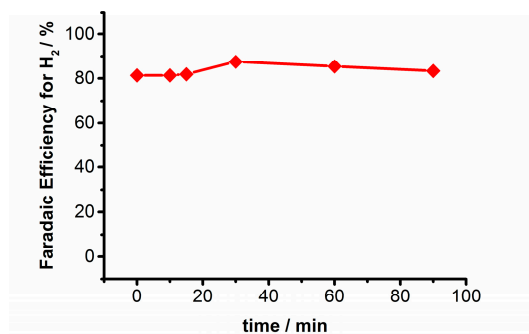


Figure S4: Hydrogen evolution in the allyl-alcohol reduction experiment.

Allyl alcohol (32 μ l, 0.47 mmol) was added after 10 min of catalyst growth time. The HER curve for the reaction doesn't show a dip after indicating a low conversion rate. This is in accordance with the low overall conversion in the as seen in the NMR. Most of the charge is still passed *via* HER.

Reduction of Propargyl Alcohol:

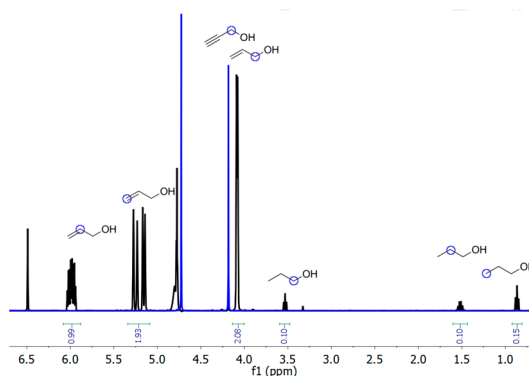


Figure S5: black: ¹H NMR spectrum of the electro reduction experiment with propargyl alcohol, blue: Reference spectrum of propargyl alcohol in D₂O.

Propargyl alcohol (blue spectrum) has been completely converted. Product spectrum (black spectrum) shows allyl alcohol and smaller signals for *n*-propanol.

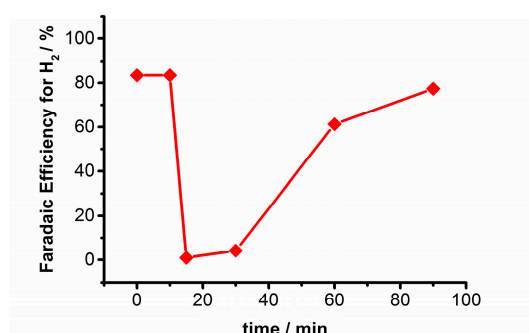


Figure S6: Hydrogen evolution in the propargyl-alcohol reduction experiment.

Propargyl alcohol (32 μ l, 0.55 mmol) was added after 10 min of catalyst growth time. Hydrogen evolution almost dropped to zero, indicating a high preference for the reduction of terminal alkynes over proton reduction. HER recovers after around 60 min when large fraction of the propargyl alcohol has been consumed.

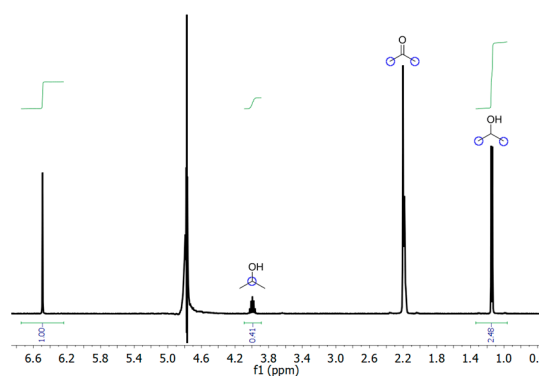


Figure S7: ^1H NMR spectrum of the electro reduction experiment with acetone (acetone reference split due to H-D exchange).

New resonances for *i*-propanol appeared, yet the spectrum still shown a large resonance for acetone indicating low conversion.

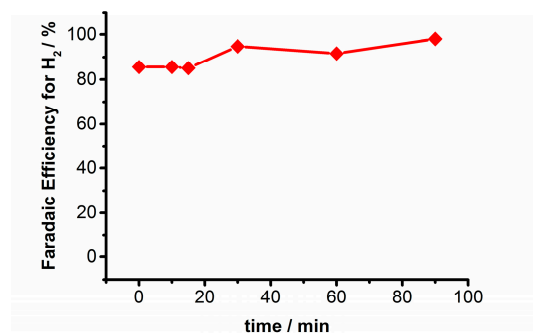


Figure S8: Hydrogen evolution in the acetone reduction experiment.

Acetone (32 μl , 0.44 mmol) was added after 10 min of catalyst growth time. Suppression of the HER is negligible due to low actual conversion.

Reduction of Potassium Fumarate:

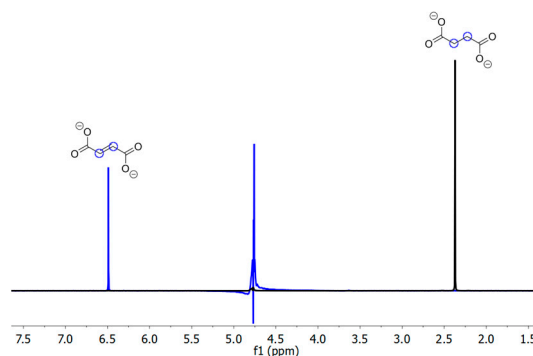


Figure S9: black: ^1H NMR spectrum of the fumarate electro reduction experiment , blue: Reference spectrum of fumarate.

The fumarate resonance (blue reference spectrum) completely disappeared indicating full conversion. The sole product of the reaction is succinate.

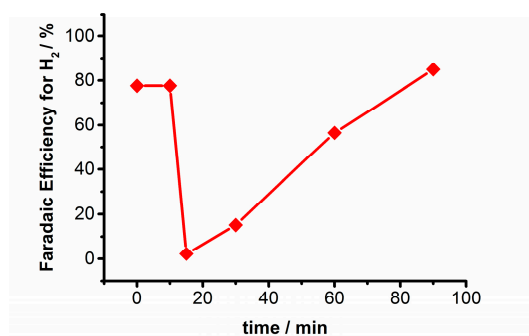


Figure S10: Hydrogen evolution in the fumarate reduction experiment.

Fumaric acid (58.7 mg, 0.51 mmol) and KOH (200 μ l 5 M, 1mmol) were added after 10 min. Initially the hydrogen evolution subsided entirely. Yet, hydrogen evolution recovers upon ongoing conversion of the fumarate.

Reduction of Mono Vinyl Acetate:

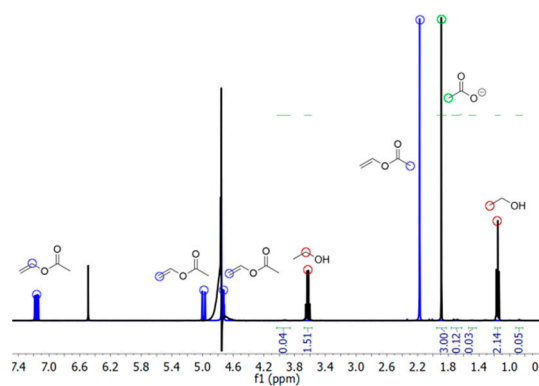


Figure S11: black: ¹H NMR spectrum of the vinyl acetate electro reduction experiment, blue: reference spectrum of vinyl acetate in D₂O.

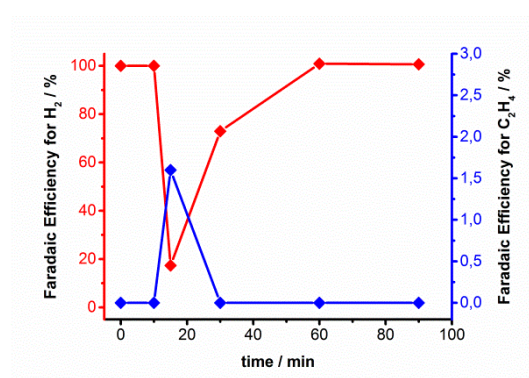


Figure S12: Hydrogen evolution in the vinyl acetate reduction experiment.

Ethylene glycol vinyl ether (32 μ l, 0.35 mmol) was added after 10 min. Hydrogen evolution was reduced to 17% in the beginning. Ethene evolution was observed shortly after the addition but was then suppressed by reduction of free acetaldehyde to ethanol.

Reduction of Mono Ethylene Glycol Vinyl Ether:

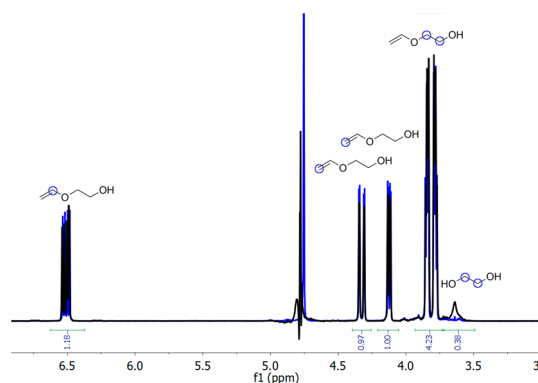


Figure S13: black: ^1H NMR spectrum of the electro ethylene glycol vinyl ether reduction experiment, blue: reference spectrum of ethylene glycol vinyl ether.

After electrolysis a new resonance for mono-ethylene glycol appeared. No other new resonances were observed.

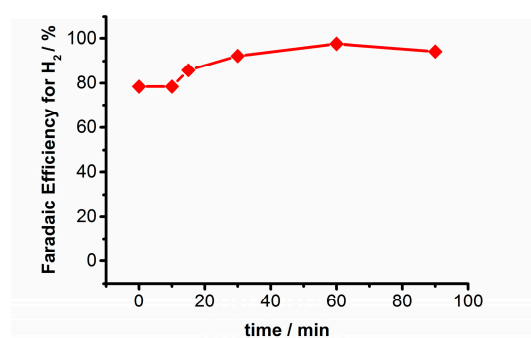


Figure S14: Hydrogen evolution in the ethylene glycol vinyl ether reduction experiment.

Ethylene glycol vinyl ether ($50\ \mu\text{l}$, $0.36\ \text{mmol}$) was added after 10 min. No significant drop was observed in the amount of hydrogen evolved.

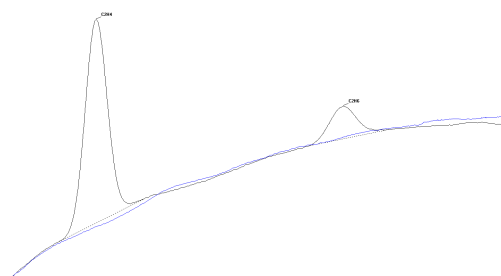


Figure S15: GC-trace of the ethylene glycol vinyl ether experiment, blue: prior to addition, black after addition.

GC analysis of the product gas showed traces of ethene and ethane. The amounts of ethene and ethane evolved fit the amounts of ethylene glycol evolved in the liquid phase. Thusly the origin of these species is the reductive cleavage of the $\text{sp}^2\text{C-O}$ bond in the vinyl ether.

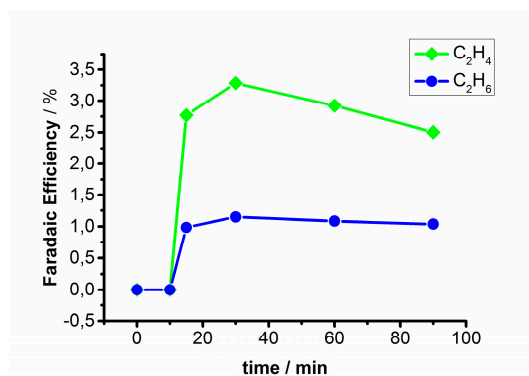


Figure S16: Faradaic efficiencies for the reductive cleavage of ethylene glycol vinyl ether. (ethene is calculated as 2e⁻-product, ethane as 4e⁻-product).

Reduction of Acetaldehyde:

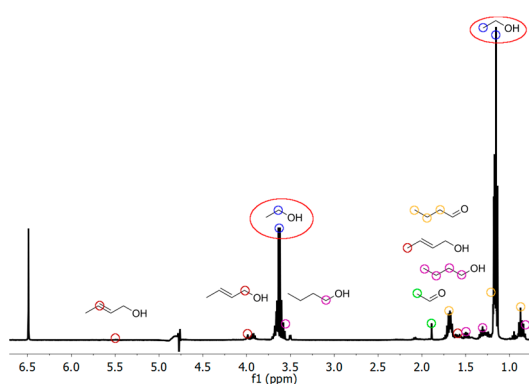


Figure S17: ¹H NMR spectrum of the electro reduction experiment with acetaldehyde (also contains a wide scope of products evolving from different combinations of aldol condensations and reductions).

Acetaldehyde was completely converted. High pH values in the cathode compartment lead to partial aldol condensation. Condensation products were also reduced. An overview of the reactions involved is depicted in **Figure S18**.

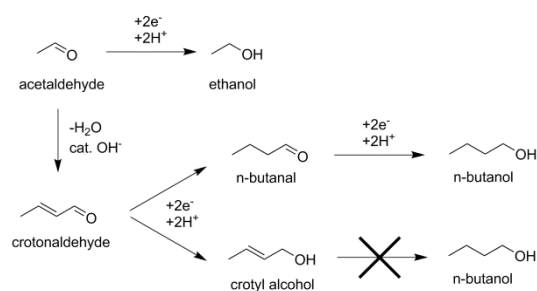


Figure S18: Schematic of the processes in an alkaline electro-reduction of acetaldehyde.

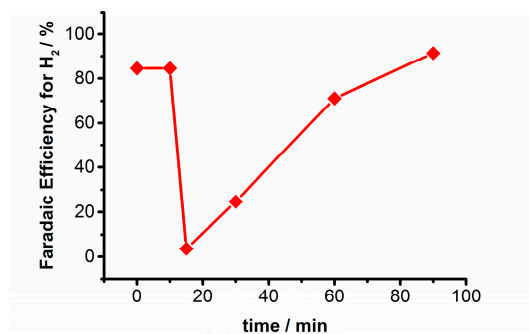


Figure S19: Hydrogen Evolution in acetaldehyde reduction experiment. Addition of acetaldehyde after 10 min.

Acetaldehyde (50 μ l, 0.90 mmol) was added after 10 min. After addition of acetic aldehyde the FE for H₂ drops to almost zero. This indicated a high hydrogenation affinity of the Cu-catalyst for acetaldehyde and supposedly also its aldol condensation products. Observation of *n*-butanol in the NMR spectrum supports this.

Reduction of Glyoxal:

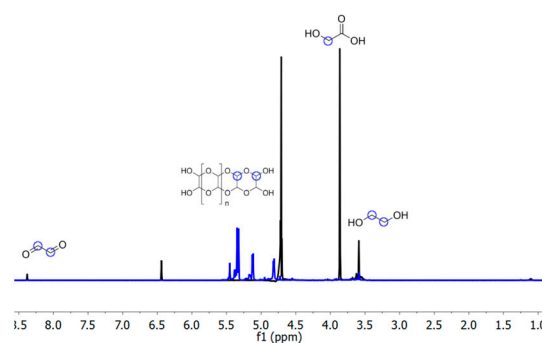


Figure S20: black: ¹H NMR spectrum of the electro reduction experiment with glyoxal blue: aqueous solution of glyoxal containing mainly cyclic acetal type oligomers.

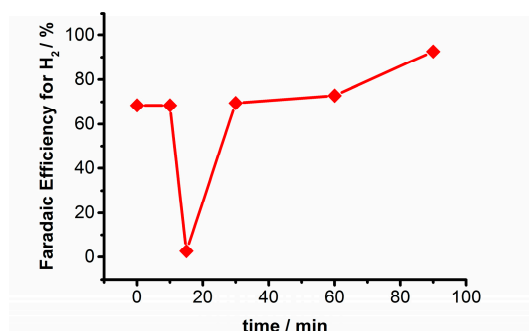


Figure S21: Hydrogen Evolution in glyoxal reduction experiment.

Glyoxal solution (125 μ l 40%, 1.1 mmol) was added after 10 min. The strong intuition suppression of the HER indicates a fast reduction of the glyoxal. Yet it recovered already after around 30 min. This is due to the rapid consumption of the glyoxal by the benzilic acid rearrangement, which proceeds in the bulk of the solution and not exclusively in the vicinity of the electrode surface.

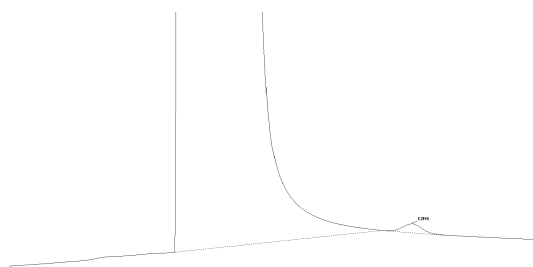


Figure S22: GC-trace of the ethene reduction experiment.

The GC spectrum shows a small peak for ethane with ethene (large peak) as feed gas. As lined out, the “reduction of alkene” section the transformation is not very efficient.

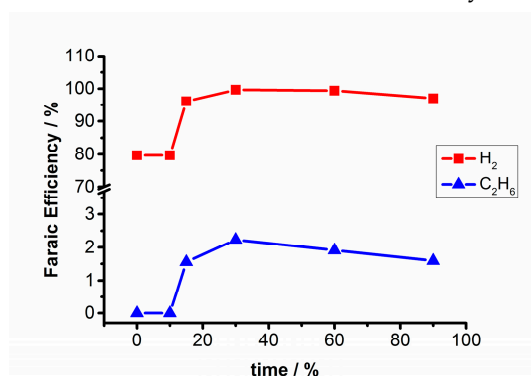


Figure S23: Faradaic Efficiencies in the ethene reduction experiment

Gas supply was switched from Ar to ethene after 10 min. Despite the large excess of ethene the maximum FE achieved for the reduction of ethene to ethane was 2.2 %.

Reduction of Ethyne:

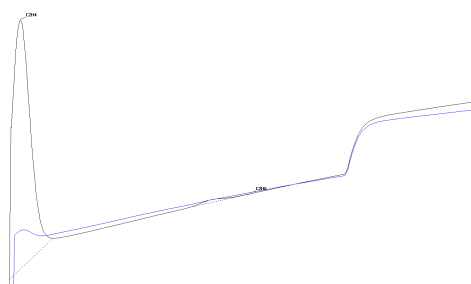


Figure S24: GC-trace of the ethyne reduction experiment: blue: reference of the used solvent free ethyne, black: trace of reduction experiment

In contrast to ethene reduction of ethyne yielded a large new peak for ethene and even a small ethane peak. A reference spectrum for the solvent free ethyne is placed in the background as also high quality ethyne isn’t entirely ethene free. Under electroreduction conditions the ethene content vastly increased.

(The drop in the baseline before the ethene peak is due to the strong interactions of ethyne with Shin-Carbon® columns).

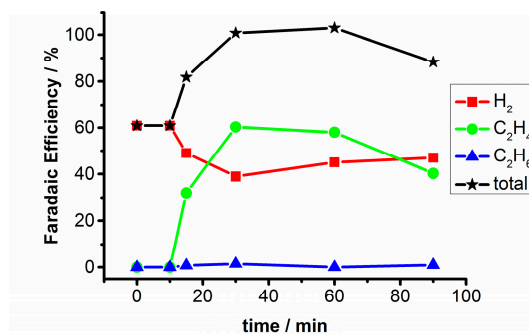


Figure S25: Faradaic efficiencies in the ethene reduction experiment (ethene is calculated as $2e^-$, ethane as $4e^-$ product).

Gas supply was switched from Ar to ethyne after 10 min. The reduction of ethyne is very efficient in compared to ethene. This additionally highlighted by the minimal evolution of ethane. This means that most of the ethene rather liberated than re-adsorbed, despite being already on the catalyst surface.

Reduction of Formaldehyde:

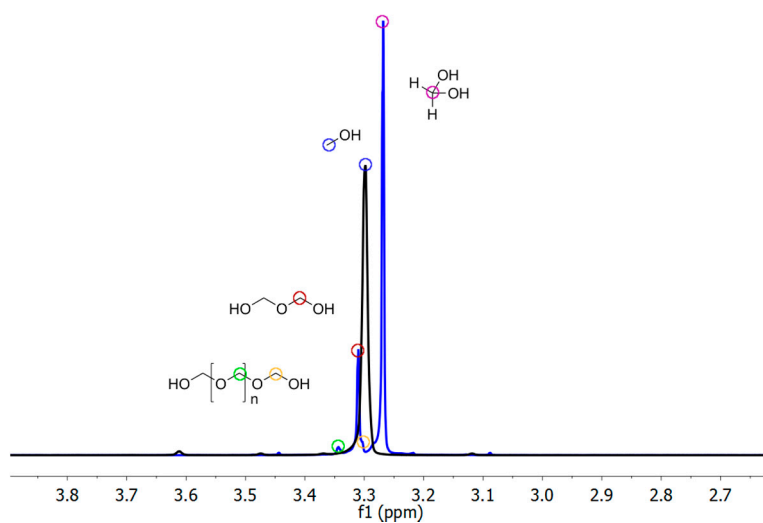


Figure S26: black: ^1H NMR spectrum of the electro reduction experiment with formaldehyde, blue: aqueous solution of formaldehyde.

Assignment of the formaldehyde spectrum was done according to Hahnenstein et al.² Importantly all formaldehyde related species vanished, while **only** methanol was formed.

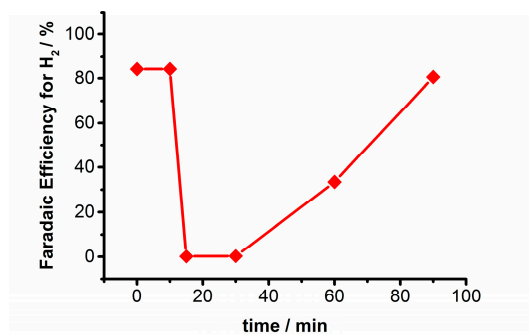


Figure S27: Hydrogen evolution in formaldehyde reduction experiment.

Formaldehyde solution (50 μ l 36%, 0.65 mmol) was added after 10 min. The HER was suppressed entirely and suppression was maintained even for lower concentrations after 30 min, indicating an even higher electro-reduction affinity for formaldehyde compare to acetaldehyde.

Reduction of 2-Butyn-1-ol:

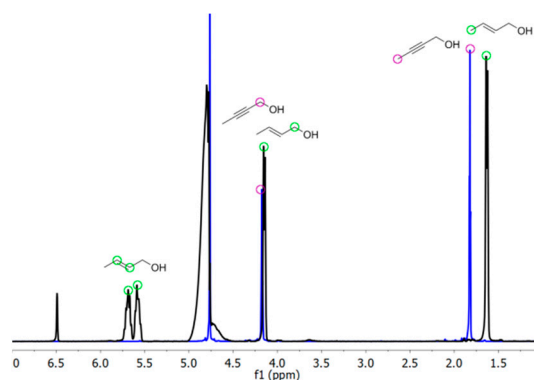


Figure S28: black: ¹H NMR spectrum of the 2-butyn-1-ol reduction experiment, black: aqueous solution of 2-butyn-1-ol.

The spectrum after electrolysis doesn't show any resonances for 2-butyn-1-ol indicating full conversion. In contrast to the propargyl alcohol experiment no n-butanol is observed.

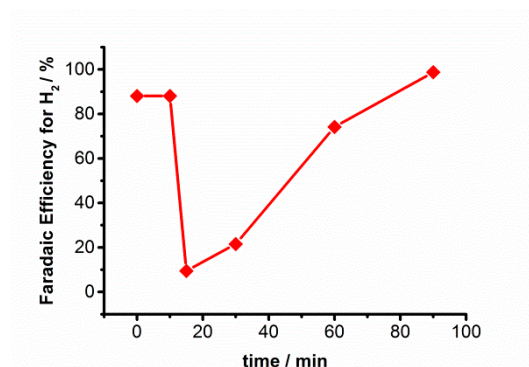


Figure S29: Hydrogen evolution in 2-butyn-1-ol reduction experiment.

2-Butyn-1-ol (32 μ l, 0.43 mmol) was added after 10 min. The GC data shows significant suppression of the HER in favor of electro-hydrogenation of the alkene. This gap is not present for electronically and sterically comparable alkenes like allyl alcohol.

Effect of substrates on working electrode potentials:

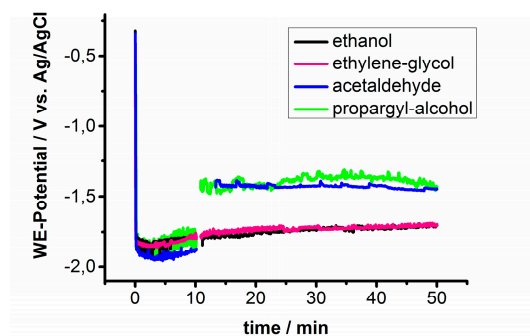


Figure S30: Working electrode potential *vs.* time plots of 4 exemplary substances from the screening.

Additions after 10 min. Reacting substrates like acetaldehyde or propargyl-alcohol lead to a sudden increase of the WE-potential.

Reduction of 1,1-dimethoxy-ethane (inert):

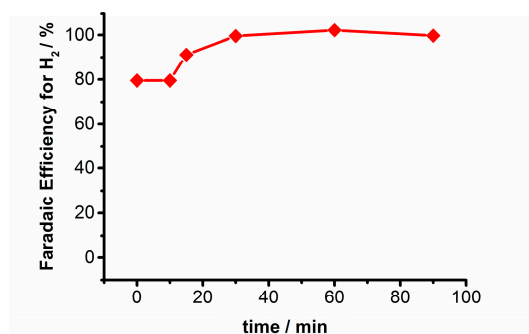


Figure S31: Exemplary hydrogen evolution curve for 1,1-dimethoxyethane (50 μ l, 0.47 mmol) as a substrate that showed no reaction, addition after 10 min.

Reduction of ethanol (inert):

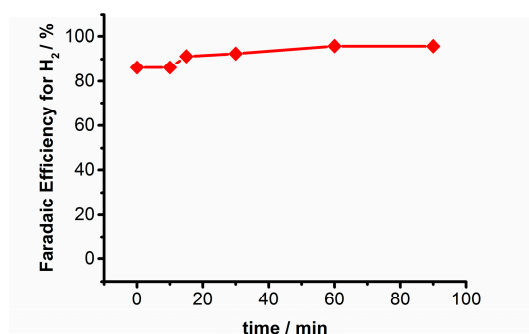


Figure S32: Exemplary hydrogen evolution curve for ethanol (50 μ l, 0.86 mmol) as a substrate that showed no reaction, addition after 10 min.

Potentiometric data for high current density bulk electrolysis experiments:

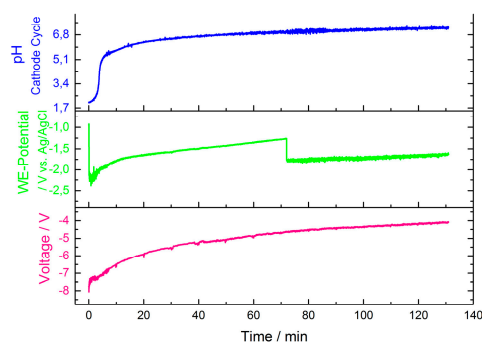


Figure S33: Electric data from the CO₂ bulk electrolysis experiment at 170 mA cm⁻².

The pH shows a rapid increase during the first minutes of electrolysis and then saturates just below 7. This is due to the CO₂/HCO₃⁻ -buffer in closed electrolyte system.

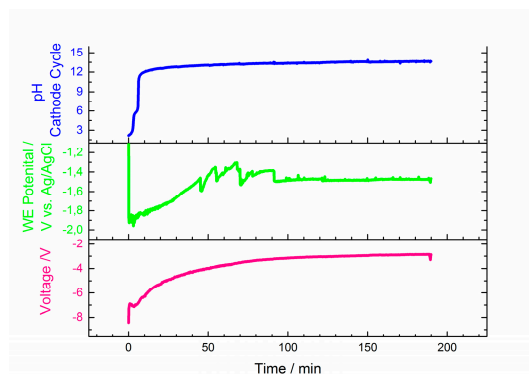


Figure S34: Electric data from the CO₂ bulk electrolysis experiment at 170 mAcm⁻².

CO gas bubbles interfere more with the Cu-GDE which indicates stronger integration. Also the WE-potential is not as stable as with CO₂. We also attribute this to the stronger interaction of CO with copper and therefore fast altering of the electrode. In absence of CO₂, there is no buffer. Thusly the pH rapidly rises to 13. An overlay of the pH curves is given in **Fig. S35**.

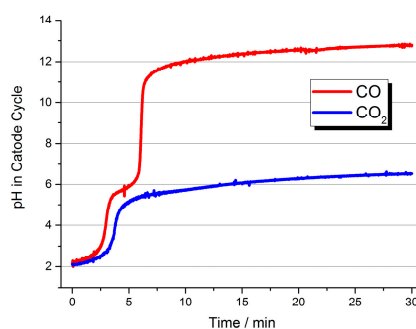
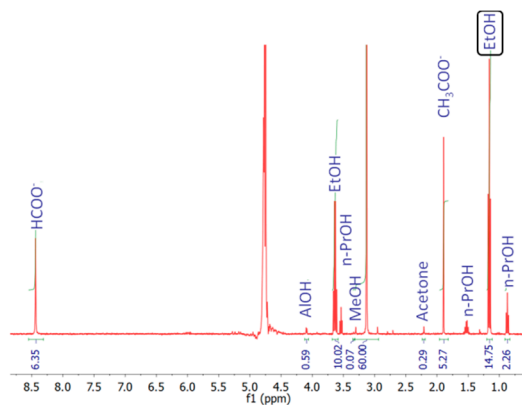


Figure S35: Comparison between the pH vs. time curves in a CO₂ and CO bulk electrolysis.

a)



b)

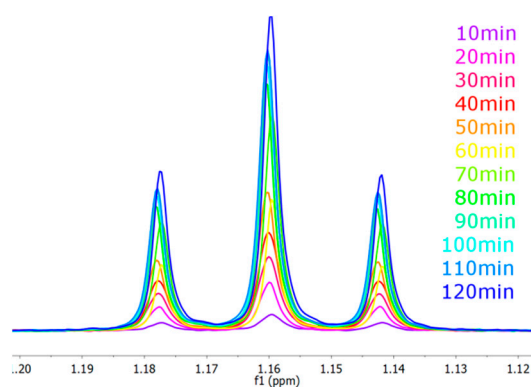


Figure S36: (a) Exemplary ^1H NMR spectrum of the electrolyte after 150 min of electrolysis (b) time resolved accumulation overlay of the ethanol C₂-resonance 10–120 min.

References

1. IKB-Feedstock-Information-Sheet: https://www.ikb.de/MediaLibrary/b1c69505-3247-4315-842e02e64fb0e1af/150305_Rohstoffpreis-Info_Q1.pdf, called 07/25/201.
2. Hahnenstein, I.; Hasse, H.; Kreiter, C. G.; Maurer, G.; ^1H - and ^{13}C -NMR Spectroscopic Study of Chemical Equilibria in Solutions of Formaldehyde in Water, Deuterium Oxide, and Methanol. *Ind. Eng. Chem. Res.* **1994**, *33*, 1022–1029.