Water and CO_2 activation at the solid/liquid interface – from Cu single crystals to compound carbide-based materials

Niusha Shakibi Nia

Linz, 28th February 2023

WIVA P&G Erfahrungsaustausch „Katalyse in CCU Prozessen“

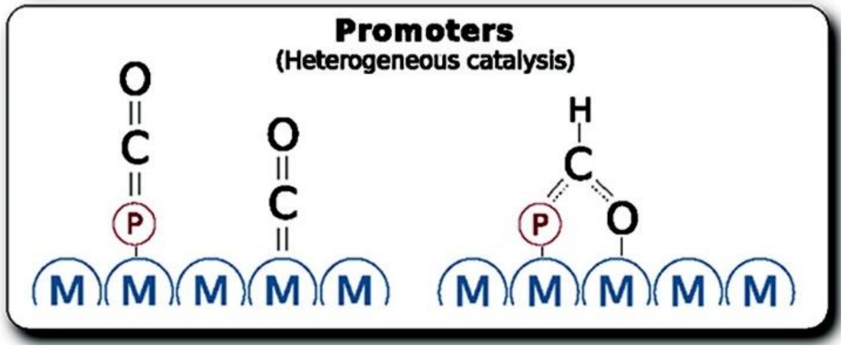
Electrochemical reduction of CO_2

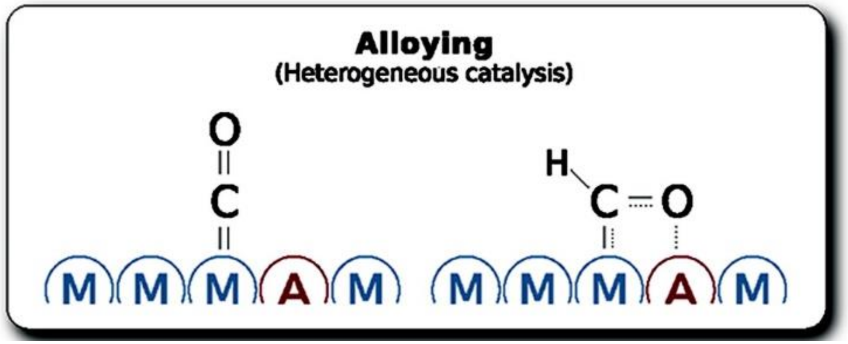
Main Challenges

- Products of CO_2R in aqueous solutions [1]:
    - **CO, formate (HCOOH), hydrocarbons (CH_4, C_2H_4) and EtOH**
    - **Slow kinetics** of CO_2 electroreduction
    - **Low energy efficiency** of the process

→ *Development of highly selective and efficient catalysts*

- **Protonation of adsorbed CO** to adsorbed CHO or COH [2]
- **Break of scaling relations** [2]





[1] A.A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J.K. Nørskov, Hydrogen Energy, Energy Environ. Sci. 3 **(2010)** 1311–1315.

[2] A.A. Peterson, J.K. Nørskov, J. Phys. Chem. Lett. 3 **(2012)**, 251–258.

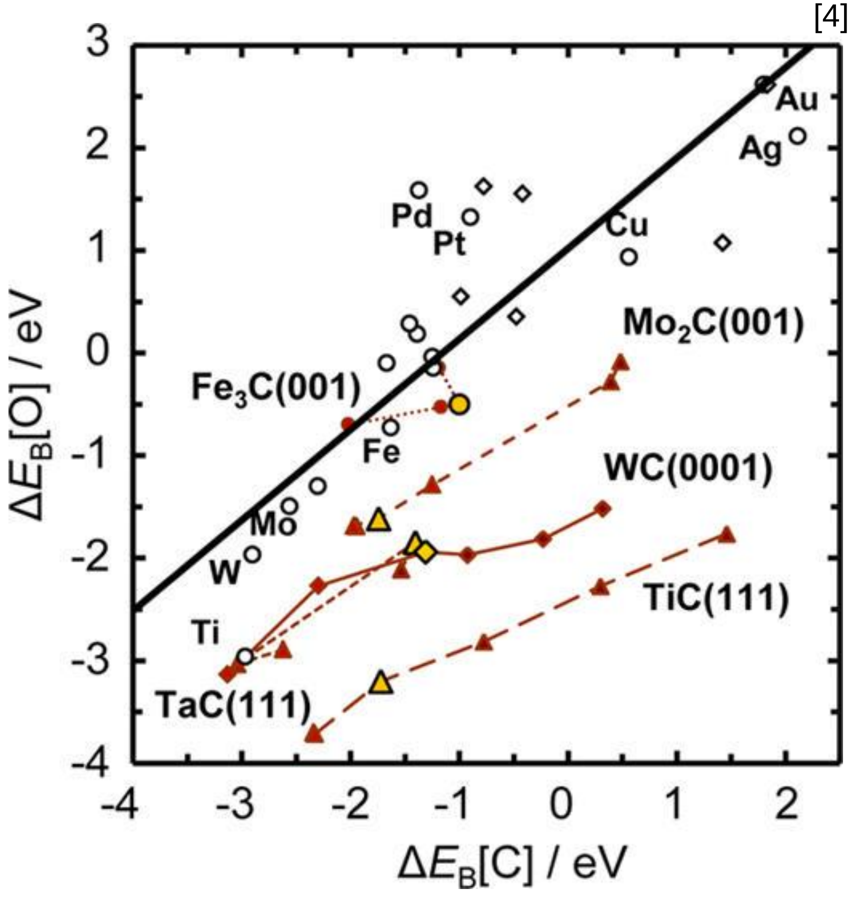
Electrochemical reduction of CO_2

Transition Metal Carbides

Green Energy Center

- C-O bond breaking on **metal carbides with a C/M < 1** [3]
- **Dynamic in catalytic operation**: Carbon vacancies [4]

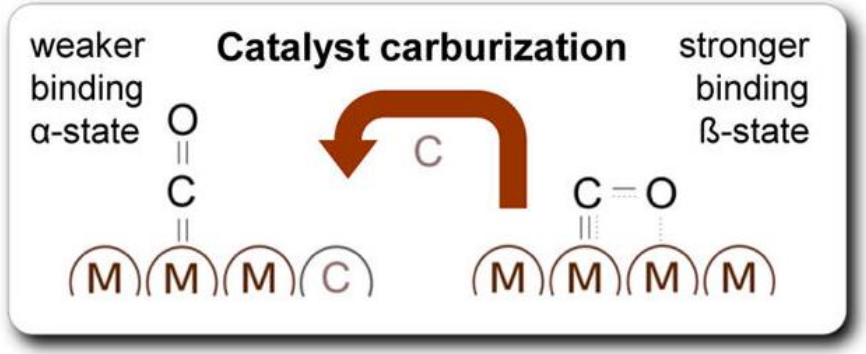
[4]



→ *Molybdenum carbide (**Mo_2C**):* [5]

- Correlation between adsorbates E_B
- H_2 dissociation
- C=O bond scission

[5]



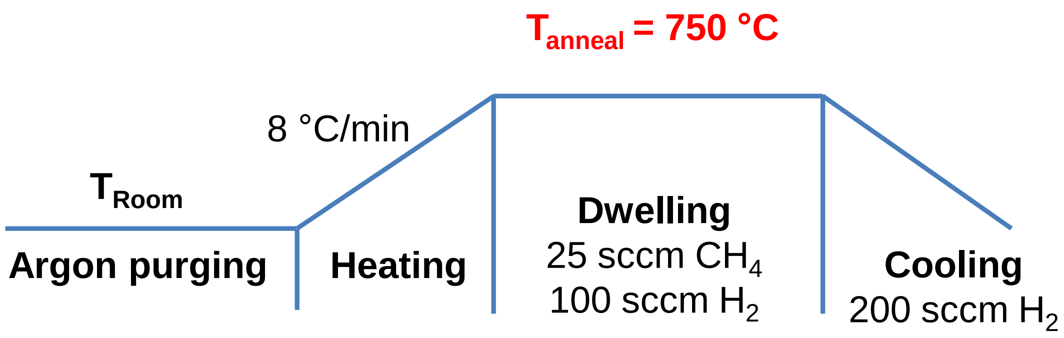
*[3] A.L. Stottlemyer, T.G. Kelly, Q. Meng, J.G. Chen, Surface Science Reports. 67 **(2012)** 201-232.*

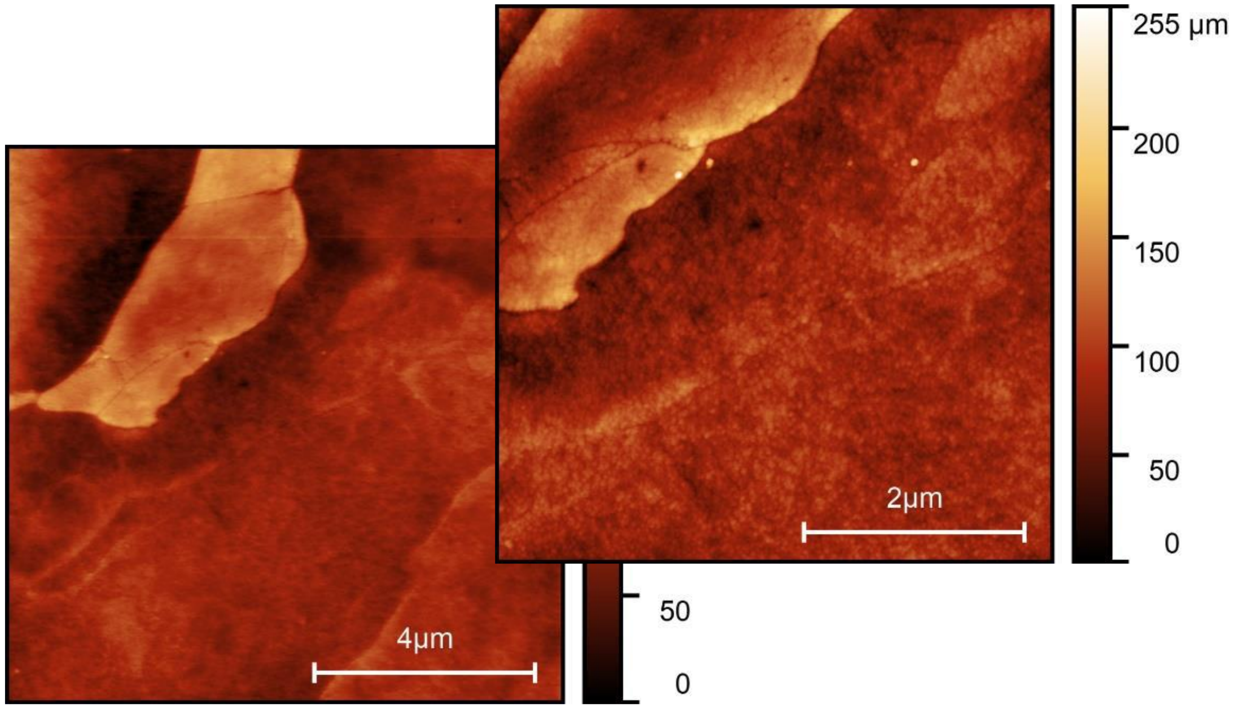
*[4] R. Michalsky,Yin-Jia Zhang, A.J. Medford, A.A. Peterson, J. Phys. Chem. C, 118 **(2014)** 13026−13034.*

*[5] A.J. Medford, A. Vojvodic, F. Studt, F. Abild-Pedersen, J.K. Nørskov, J. Catal. 290 **(2012)**, 108-117.*

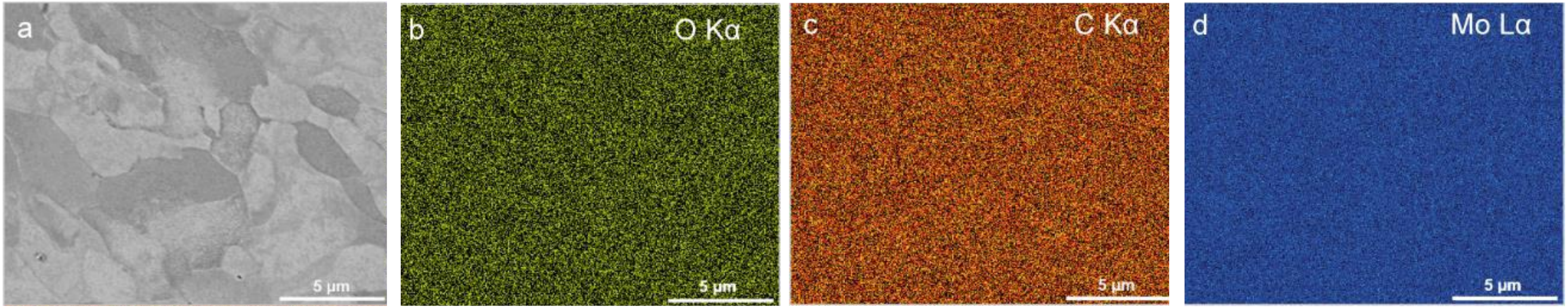
Planar Mo_2C Films

Synthesis & Characterization [6]





- Surface topography:
  - **Several micrometer wide terraces**
  - Surface **chemical homogeneity**

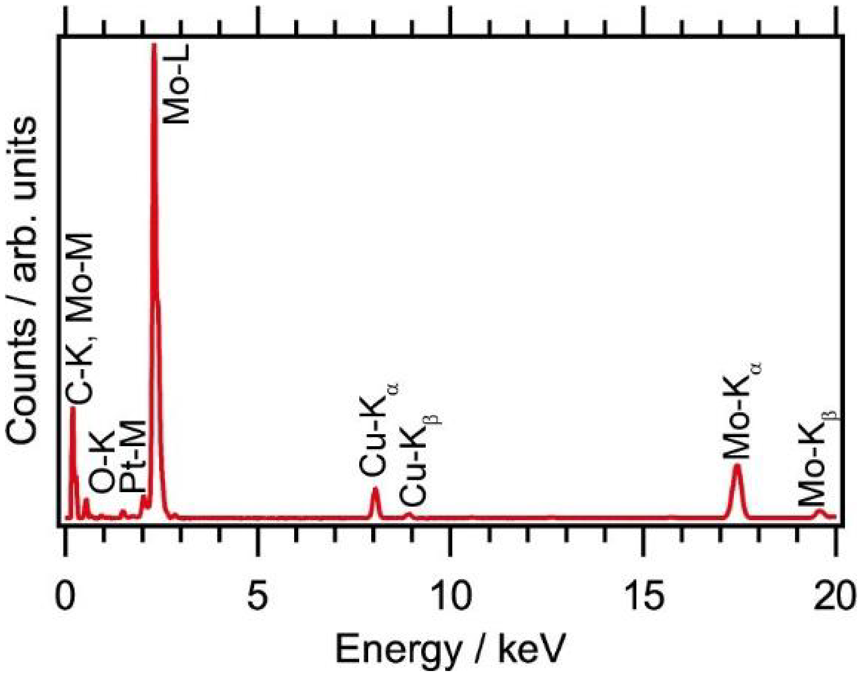


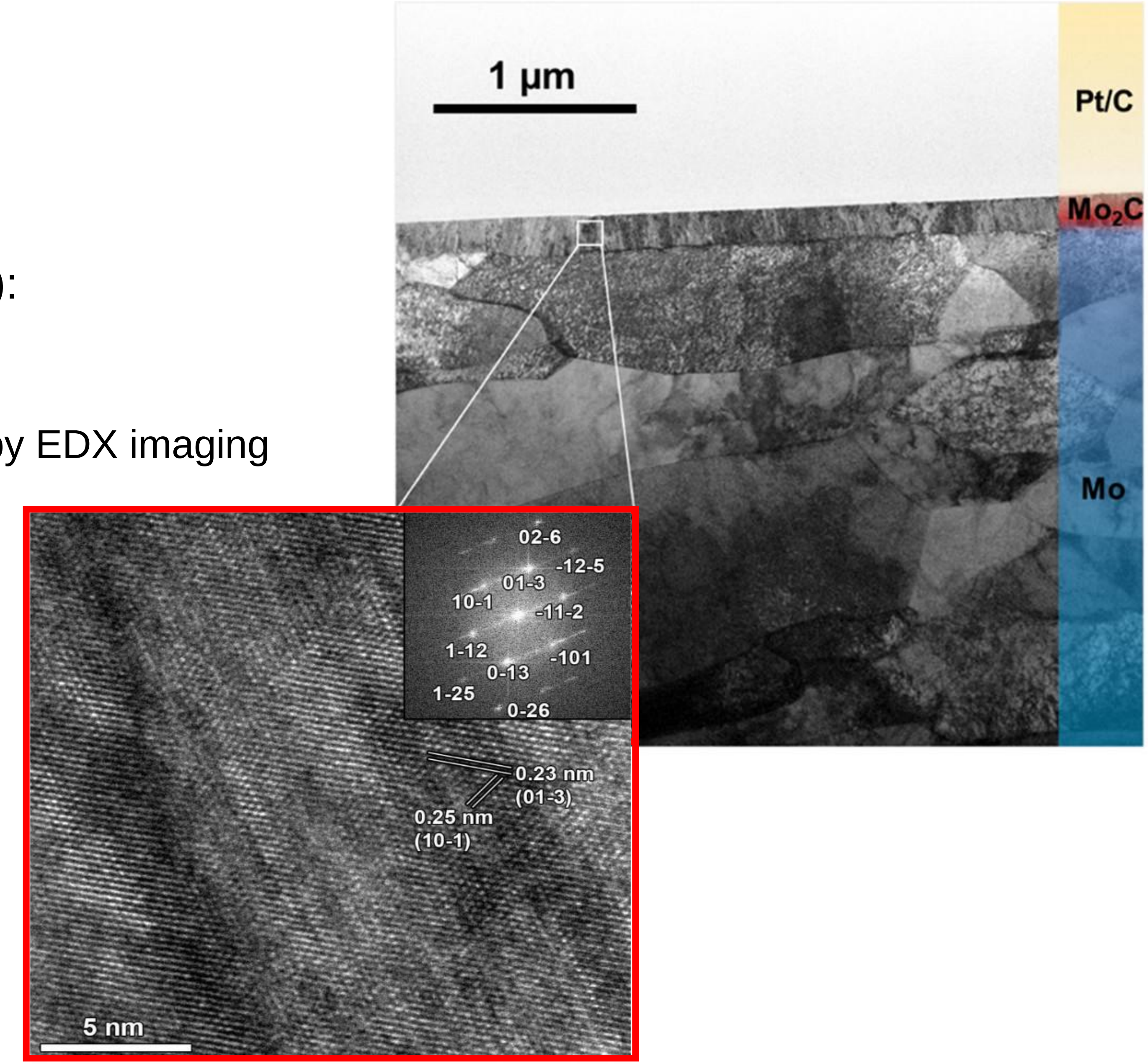
[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

Cross-Sectional Characterization [6]

- **Homogenous film** in thickness
- Multiple crystal structure testing (CrysTBox):
    - **Hexagonal** with carbon deficient structure
    - **Molybdenum-to-carbon ratio** verification by EDX imaging



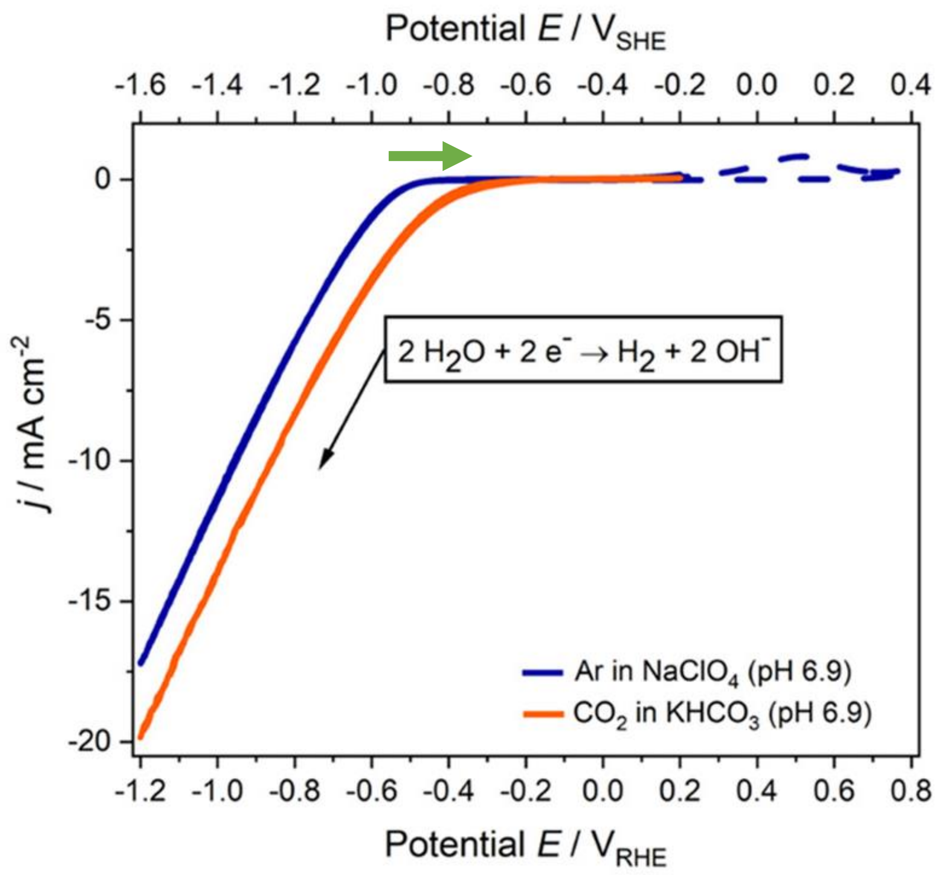


[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

Electrocatalytic Performance [6]

- Oxidation of electrodes at E > − 0.2 V_{SHE}
- Onset of H_2O reduction in CO_2 saturated electrolyte slightly shifted

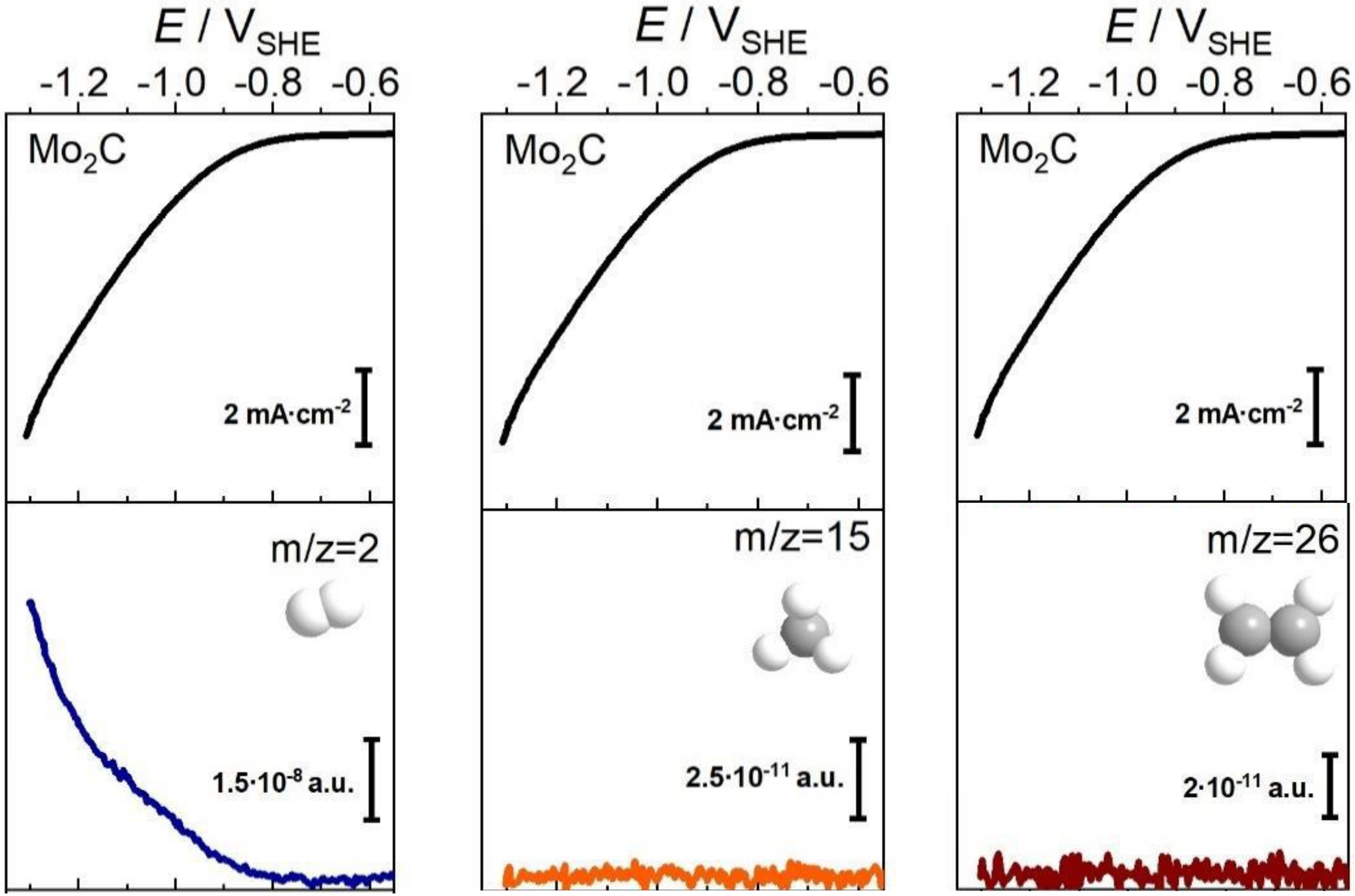


[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

Qualitative Identification of CO_2R Reaction Products [6]

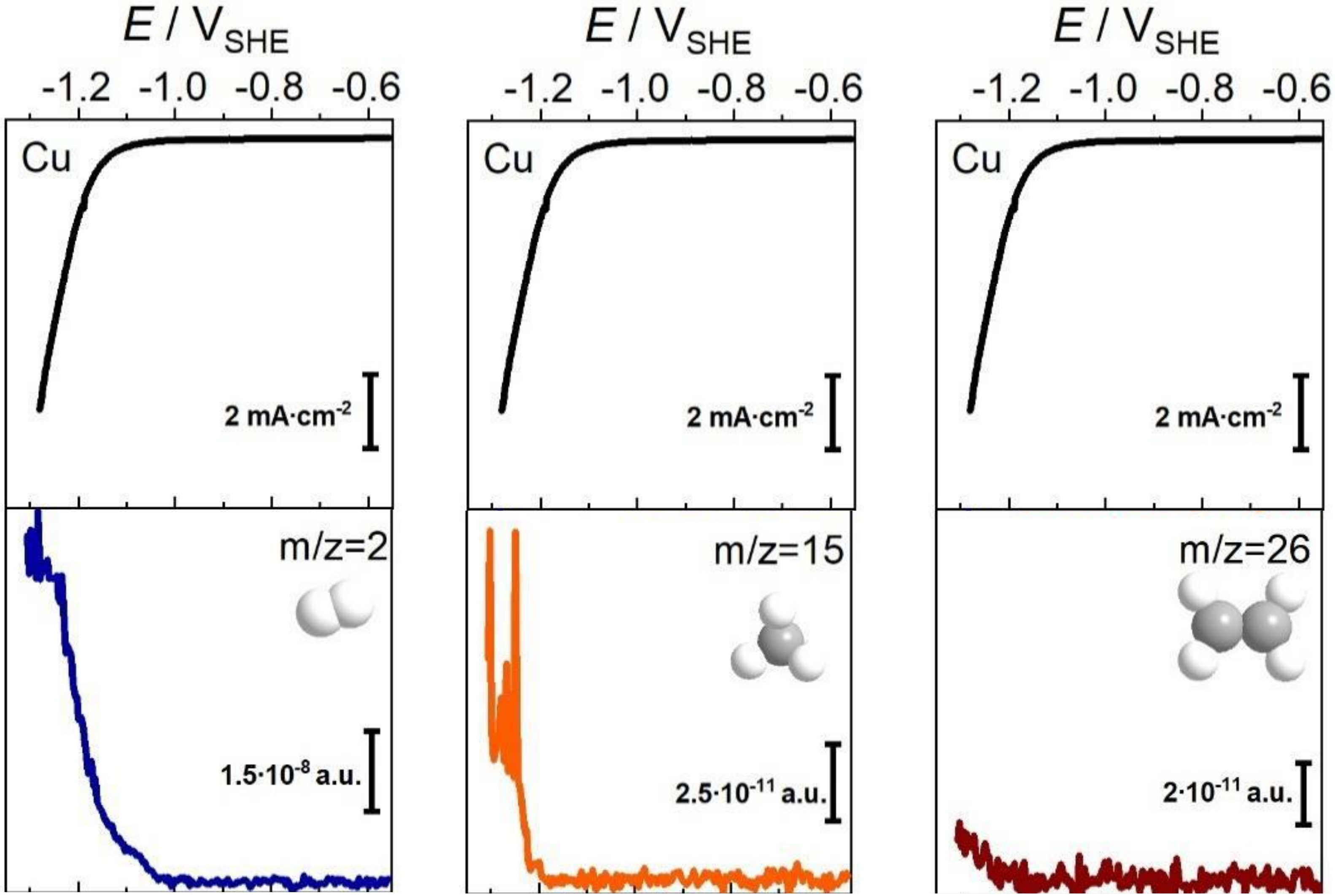
Green Energy Center



[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

Qualitative Identification of CO_2R Reaction Products [6]



[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

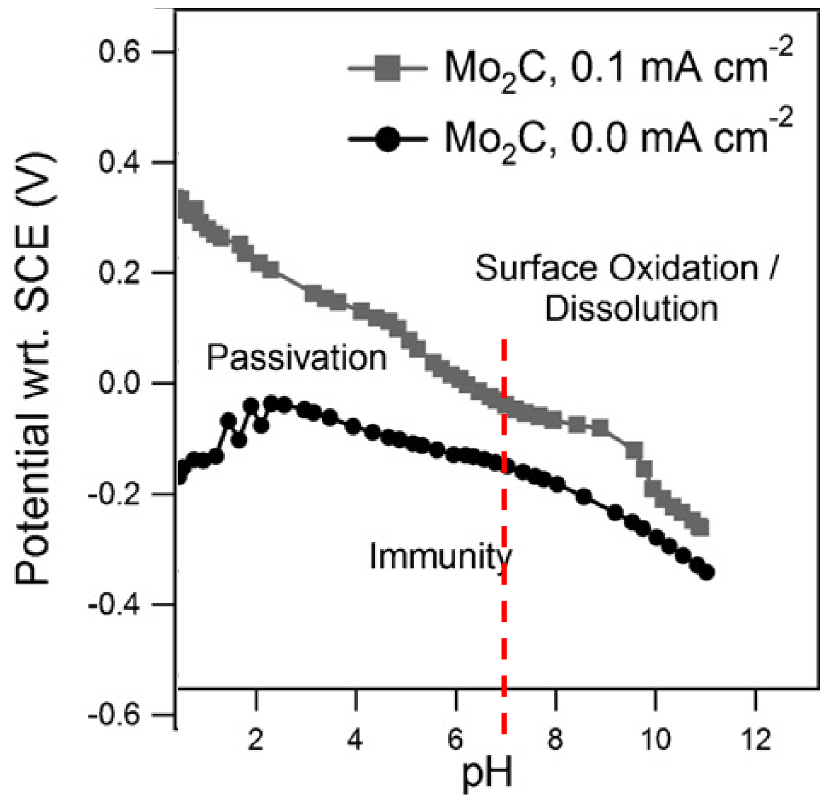
Planar Mo_2C Films

Thermodynamics of Mo_2C in Aqueous Electrolyte [6]

Green Energy Center

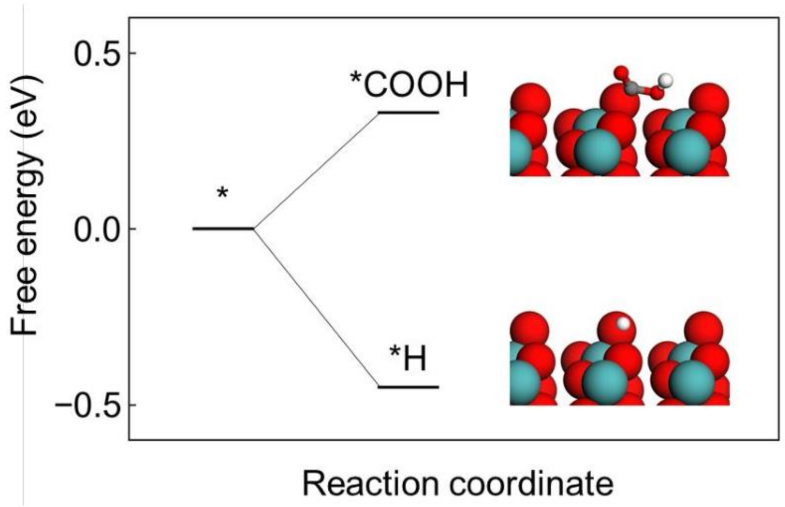
- No CO_2 electroreduction with Mo_2C planar films → Thermodynamic stability of surface oxides?

[7]



→ *DFT-based ab initio thermodynamics* [6]

- ○ Higher overpotentials are required to reduce the surface
- ○ First protonation step of the HER and CO_2RR
  - $MoO_2(100)$ covered $Mo_2C(110)$ surface



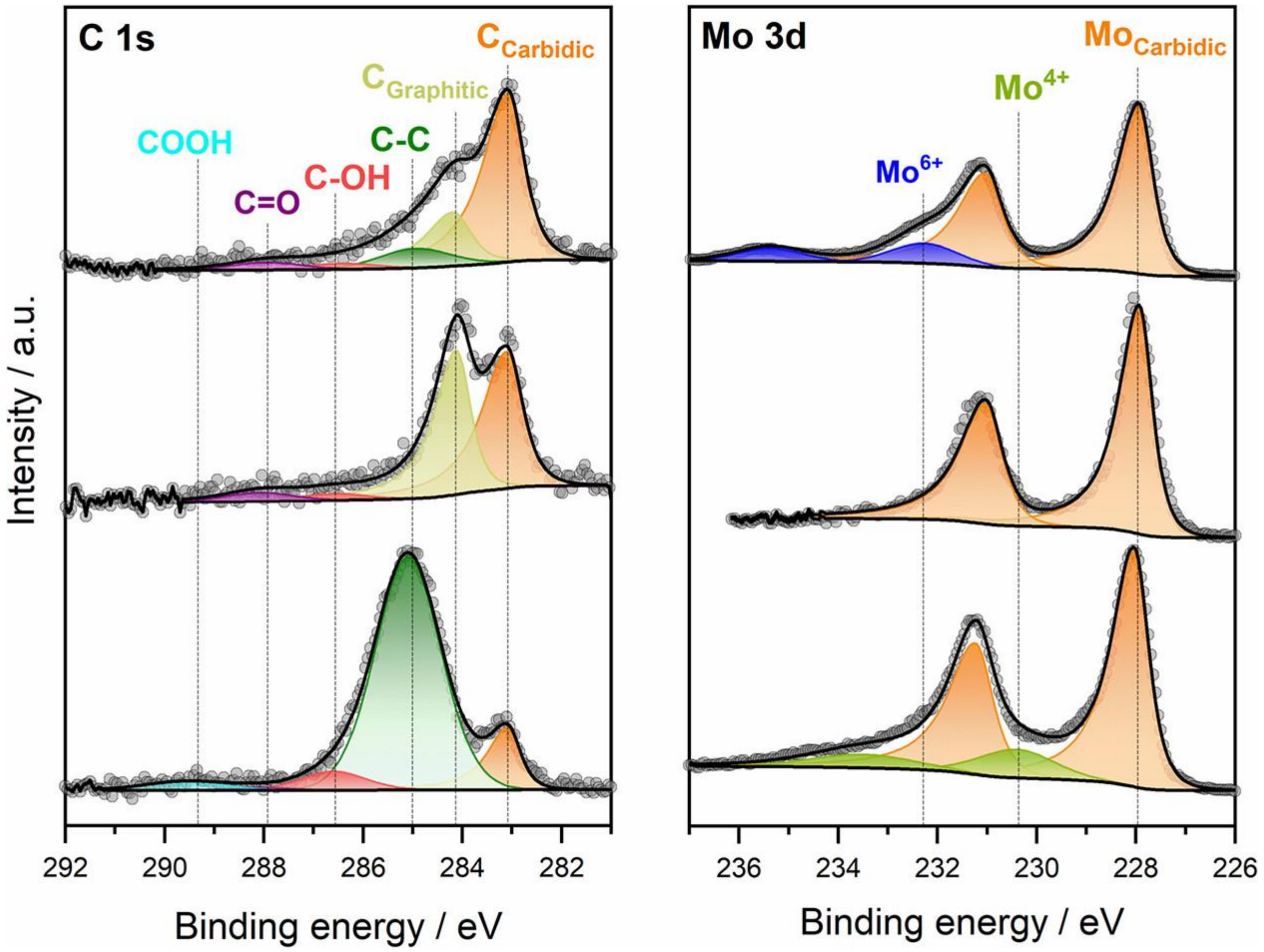
[7] *Weidman, M. C. et al. Comparison of Electrochemical Stability of Transition Metal Carbides, J. Power Sources 2012, 202, 11−17.*

[6] *Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal.* ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

Analysis of Chemical Composition [6]

Green Energy Center



*Mo_2C after a **15 min air contact***

***Oxide-free** Mo_2C*

*After **immersion** of the **oxide-free** Mo_2C in the electrolyte*

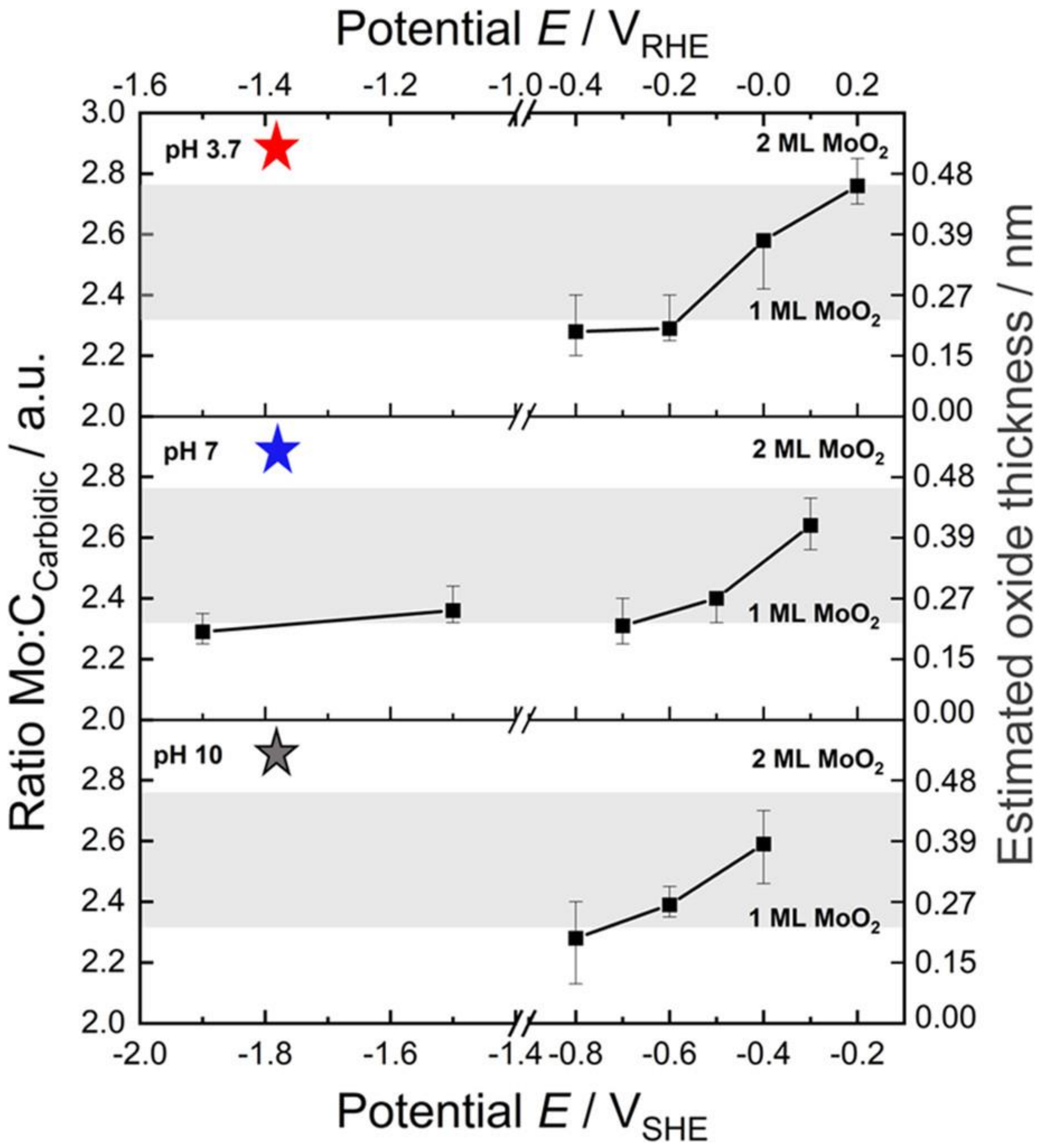
→ *Absolute impossibility to start from an oxide- or oxygen-free catalyst/electrolyte interface!*

*[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. **2021**, 11 (8), 4920–4928.*

Planar Mo_2C Films

Experimental Pourbaix Diagram [6]

- Recording of XPS spectra after potentiostatic polarization:
  - Calculation of Mo/$C_{carbidic}$ ratio
  - Oxide layer thickness estimation
- Stepping to more negative potentials
  - Oxide film thickness decrease
  - **pH 7: oxide film stability at lower potentials**
- Comparison with **CO_2RR conditions**
  - Polarization at − 0.4 and − 1.5 V_{SHE}
    - → *Similar thin surface oxide films formation*



[6] *Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal.* ***2021****, 11 (8), 4920–4928.*

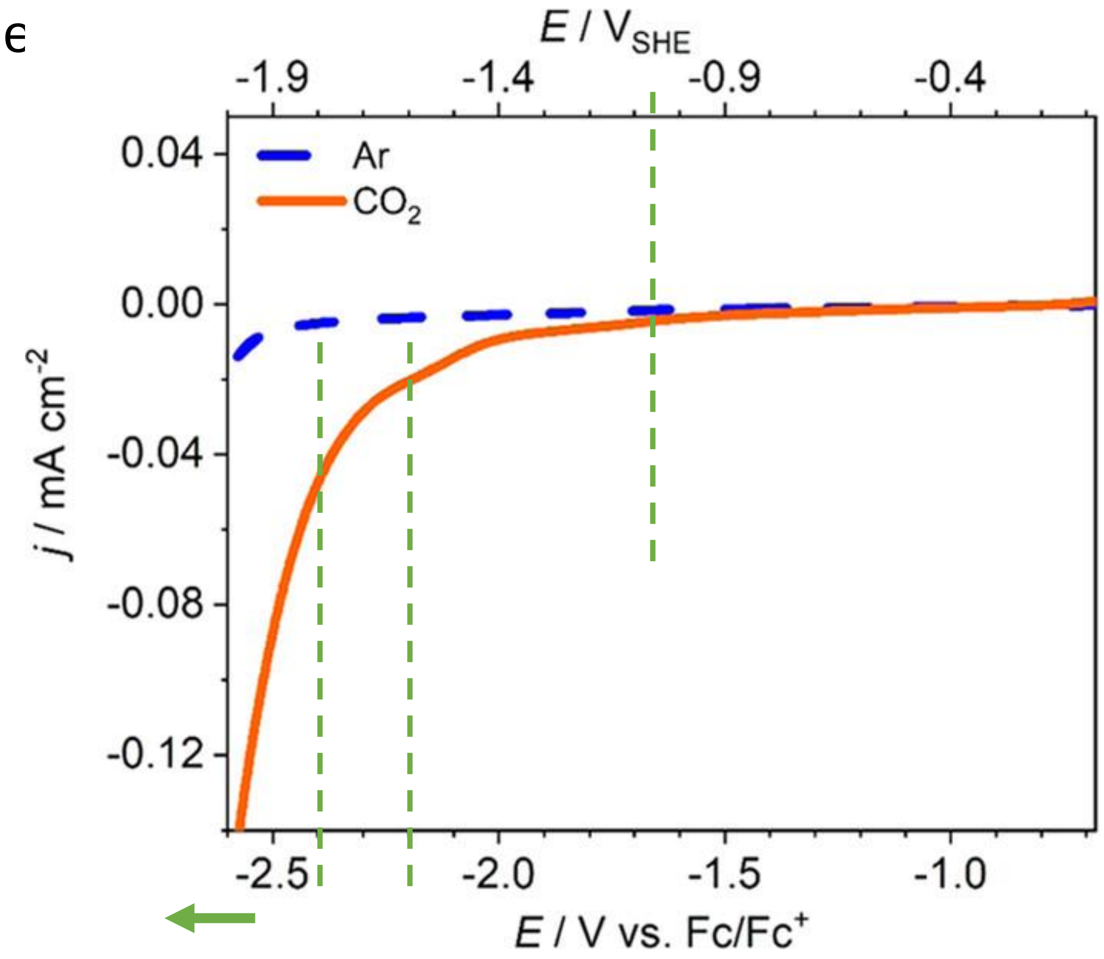
Planar Mo_2C Films

CO_2 Electroreduction in Nonaqueous Electrolyte [6]

- **Proof-of-principle experiments** in acetonitrile-based e
  - CO_2R onset at − 1.08 V_{SHE}
  - Polycrystalline Cu
    - ~ CO_2R onset at − 1.31 V_{SHE} (same electrolyte)
  - No reduction peak visible in Ar-purged electrolyte

→ *In situ electrochemical infrared spectroscopy*

- **CO formation at ≤ − 1.9 V_{SHE}!**

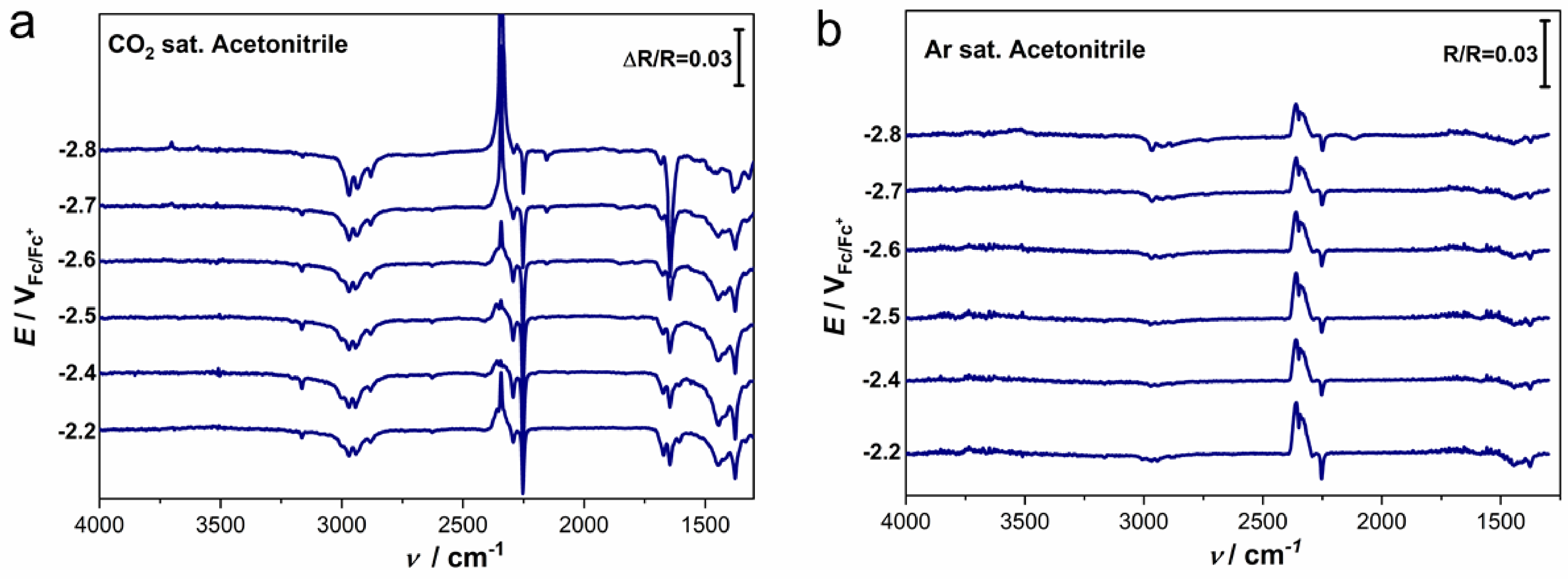


[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. **2021**, 11 (8), 4920–4928.

Planar Mo_2C Films

CO_2 Electroreduction in Nonaqueous Electrolyte [6]

Green Energy Center

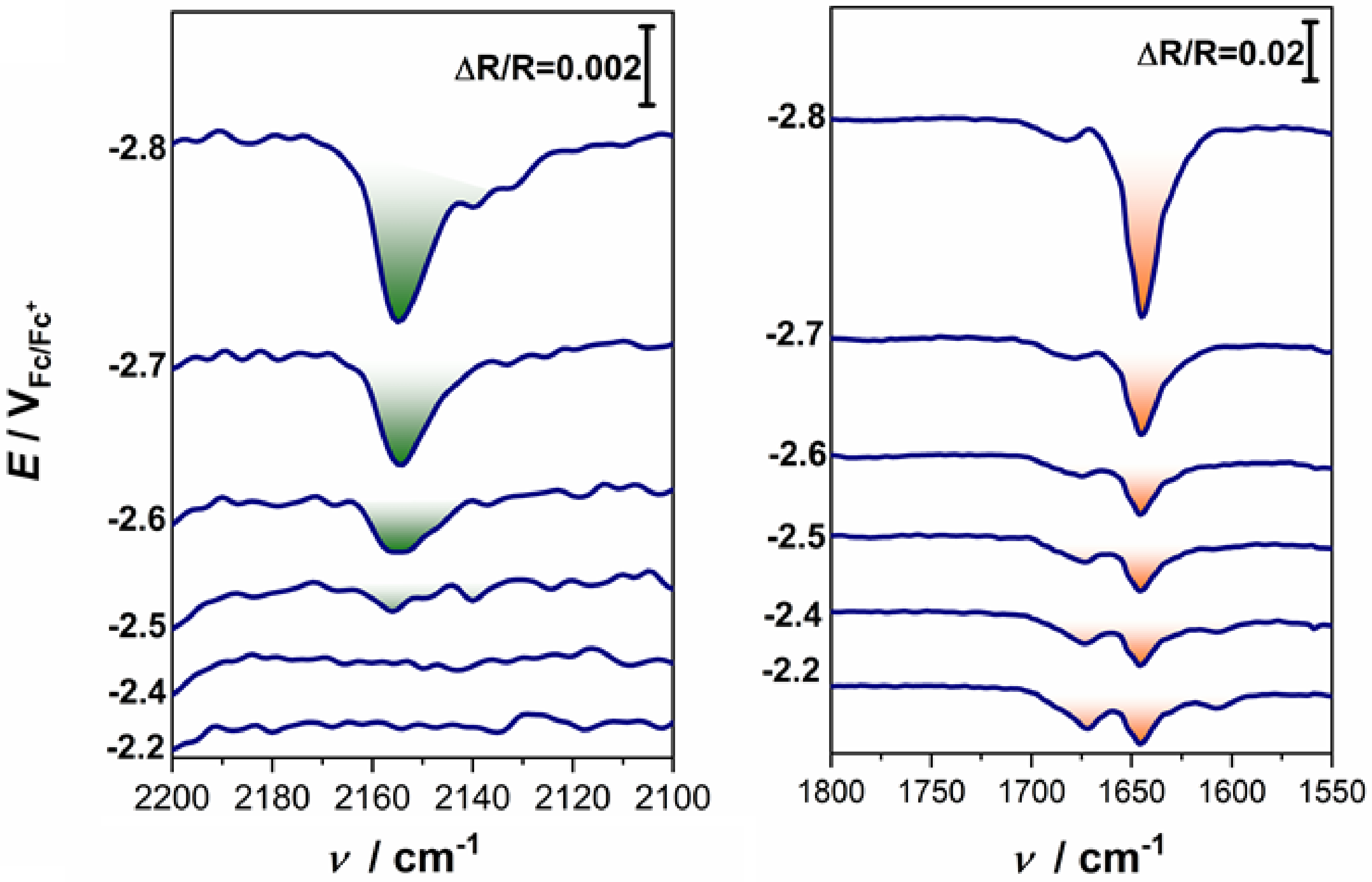


[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal. ***2021****, 11 (8), 4920–4928.*

Planar Mo_2C Films

CO_2 Electroreduction in Nonaqueous Electrolyte [6]

- CO_2 reduction product formation:
  - **CO formation** at ~ 2158 cm^{-1}
  - **Oxalate and carbonate formation** between 1600 cm^{-1} & 1700 cm^{-1}



[6] Griesser, C.; Li, H.; Wernig, E. M.; Winkler, D.; Shakibi Nia, N.; Mairegger, T.; Götsch, T.; Schachinger, T.; Steiger-Thirsfeld, A.; Penner, S.; Wielend, D.; Egger, D.; Scheurer, C.; Reuter, K.; Kunze-Liebhäuser, J. *True Nature of the Transition-Metal Carbide/Liquid Interface Determines Its Reactivity. ACS Catal.* ***2021****, 11 (8), 4920–4928.*

Electrochemical reduction of CO_2

Product Selectivity

- Metal electrodes → **formate** [8,9], **carbon monoxide**, and **hydrogen** (from water)
- Copper electrodes → **further products**: **sufficient efficiencies** but **undesirable selectivity** [9,10]
  - Most desirable products: Alcohols (e.g., **methanol**) [11]
  - **Challenging** direct electrochemical **CO_2R to methanol**: **methane** or **ethylene** preferential formation [8]
    - → *Conversion of **formic acid (**generated from CO_2) to methanol*
    - → *Formic acid electroreduction at **transition metal oxides***
      - *Electrochemically stable*
      - *Favorable adsorption of formic & acetic acid*

*[8] J. Qiao, Y. Liu, F. Hong, J. Zhang, Chem. Soc. Rev. **2014**, 43(2), 631–675*
*[9] S. Nitopi, E. Bertheussen, S. B. Scott, X. Liu, A. K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Norskov, T. F. Jaramillo, & Chorkendorff, I., Chem. Rev. **2019**, 119(12), 7610–7672*
*[10] Y. Hori, Handbook of Fuel Cells; John Wiley & Sons, Ltd: Chichester, UK, **2010**, pp 1–14*
*[11] S. S. Munjewar, S. B. Thombre, R. K. Mallick, Ionics (Kiel). **2017**, 23(1), 1–18*

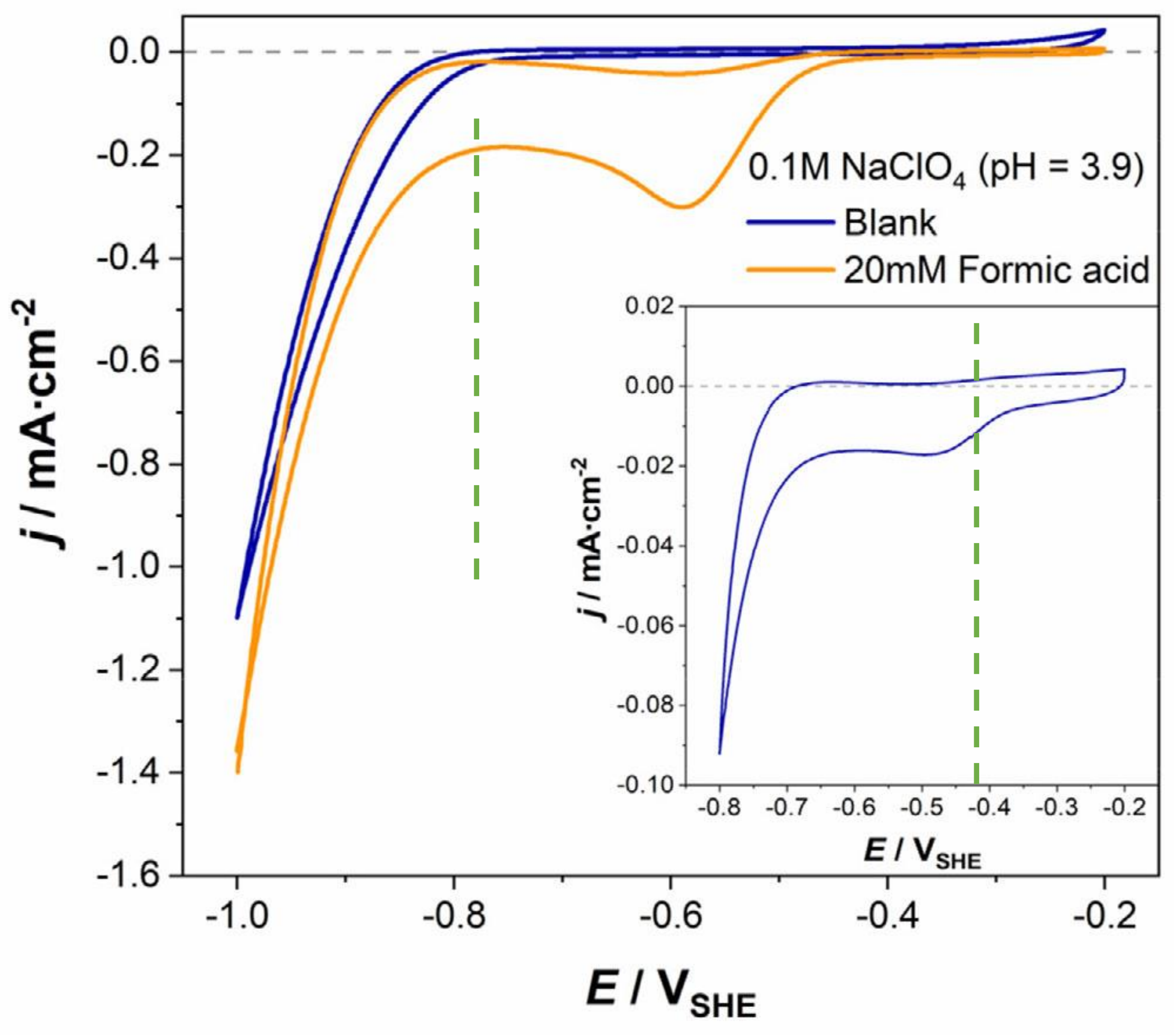
Planar Mo_2C Films

Formic Acid Electroreduction in Acidic Media [12]

Green Energy Center

- High cathodic current densities at – 1.0 V_{SHE}
- **HER** activity:
  - **Proton reduction** onset at – 0.43 V_{SHE}
  - **H_2O reduction** at – 0.76 V_{SHE}
- Comparable shape of CVs
- **Difference in current densities** by an order of magnitude

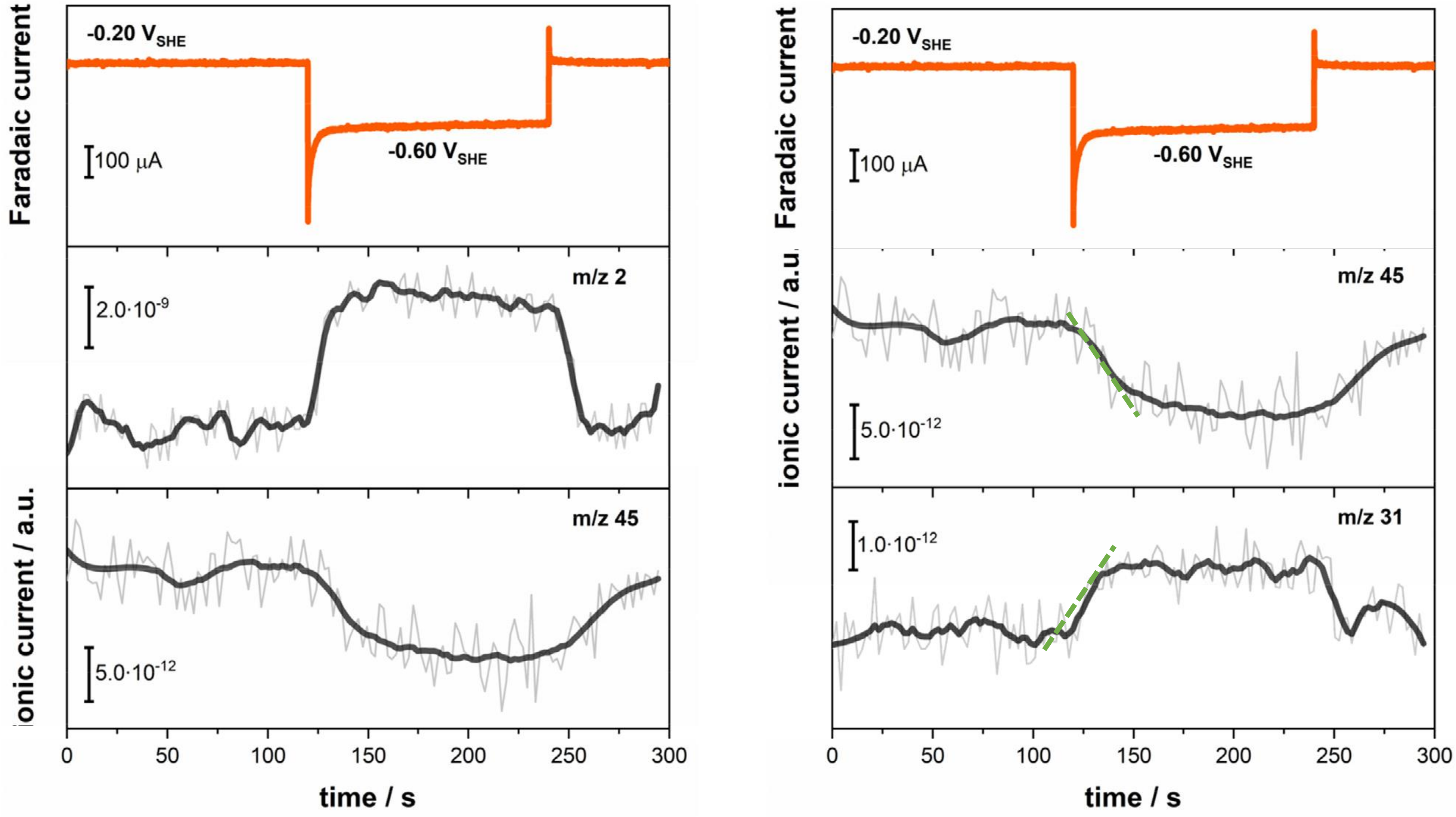
→ *Identification of reduction products*



[12] Winkler, D.; Dietrich, V.; Griesser, C.; Shakibi Nia, N.; Wernig, E.-M.; Tollinger, M.; Kunze-Liebhäuser, J. Formic Acid Reduction and CO2 Activation at Mo 2 C: The Important Role of Surface Oxide. Electrochem. Sci. Adv. ***2022****, 2 (3), e2100130.*

Planar Mo_2C Films

Formic Acid Electroreduction Products [12]

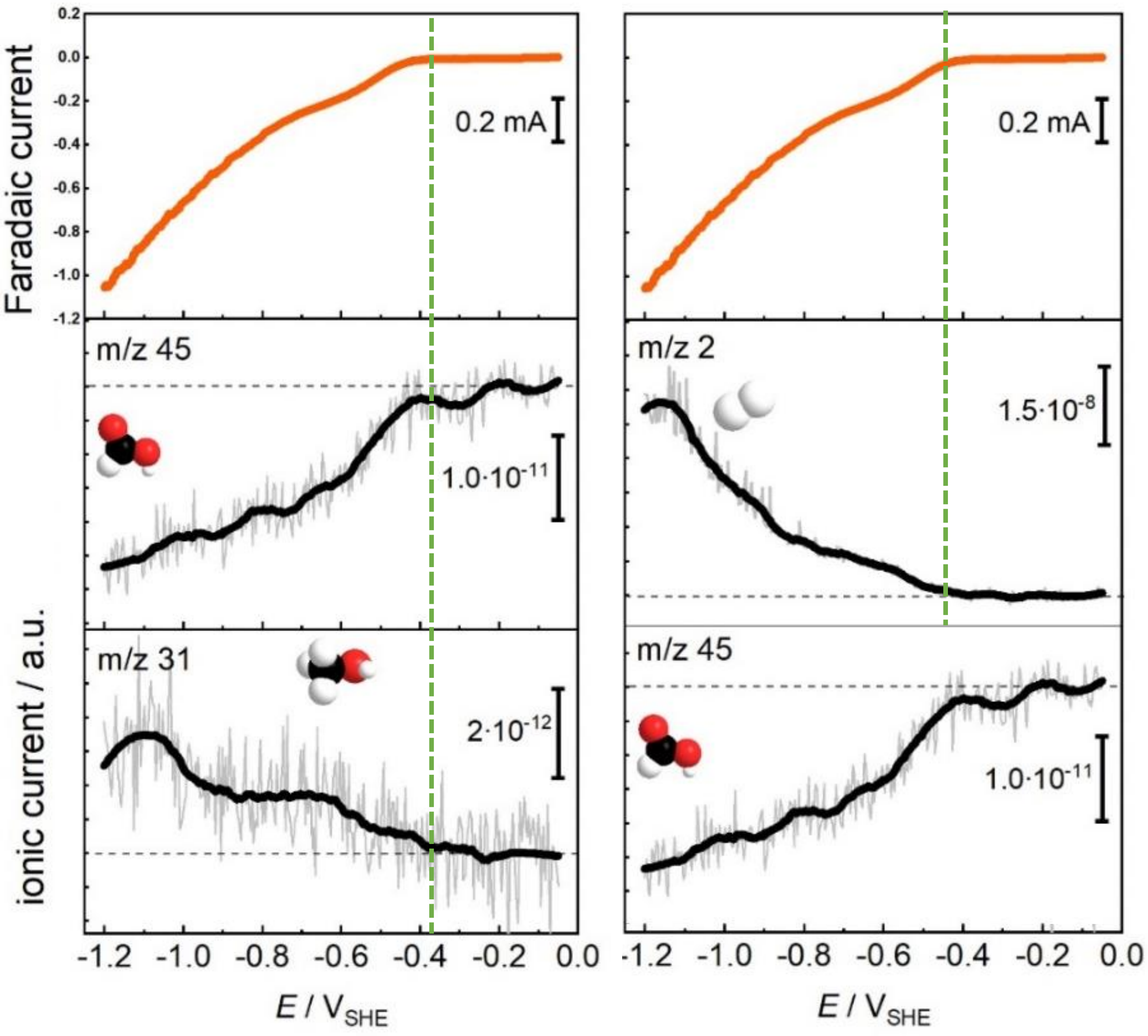


[12] Winkler, D.; Dietrich, V.; Griesser, C.; Shakibi Nia, N.; Wernig, E.-M.; Tollinger, M.; Kunze-Liebhäuser, J. Formic Acid Reduction and CO2 Activation at Mo 2 C: The Important Role of Surface Oxide. Electrochem. Sci. Adv. ***2022****, 2 (3), e2100130.*

Planar Mo_2C Films

Formic Acid Electroreduction Products [12]

- Onset of hydrogen formation – 0.44 V_{SHE}
- Onset of methanol formation – 0.39 V_{SHE}
  - Formation rate increase with potential
- Methanol formation confirmed by NMR spectroscopy
  - Faraday efficiency of ~27 % at – 0.60 V_{SHE}



[12] Winkler, D.; Dietrich, V.; Griesser, C.; Shakibi Nia, N.; Wernig, E.-M.; Tollinger, M.; Kunze-Liebhäuser, J. Formic Acid Reduction and CO2 Activation at Mo 2 C: The Important Role of Surface Oxide. Electrochem. Sci. Adv. ***2022****, 2 (3), e2100130.*

Conclusions

Green Energy Center

- Well-defined **planar hexagonal Mo_2C films**:
  - Intrinsic **surface passivation** upon:
    - → air exposure (**MoO_3**)
    - → immersion in aqueous electrolyte (ultrathin **MoO_2** that remains at the interface)
    - → Interface chemistry enhances the **organic acid reduction activity**
    - → **Formic acid** electroreduction to **methanol**
  - CO_2 Electroreduction in *aqueous electrolyte*
    - → activity towards **water reduction**
    - → **no CO_2 electroreduction products**
  - CO_2 Electroreduction in *nonaqueous electrolyte*
    - → **CO_2 electroreduction to gaseous CO**

Acknowledgments

Green Energy Center

universität innsbruck

Institute of Physical Chemistry

Univ.-Prof. Dr. Julia Kunze

Eva-Maria Wernig, MSc.

Christoph Grießer, MSc.

Daniel Winkler, MSc.

Thomas Mairegger, MSc.

fen research

Green Energy Center