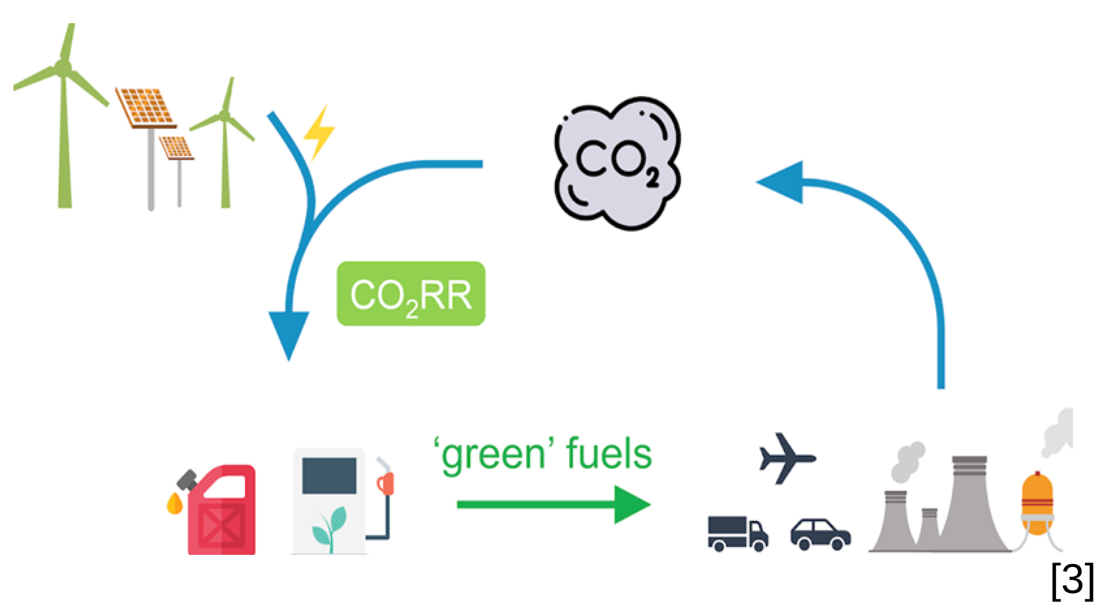
Sustainable Design of Copper-based CO_2 Electrolyzers

Victor D. Brandão and Carsten Sievers
School of Chemical and Biomolecular Engineering, Georgia Institute of Technology

Background

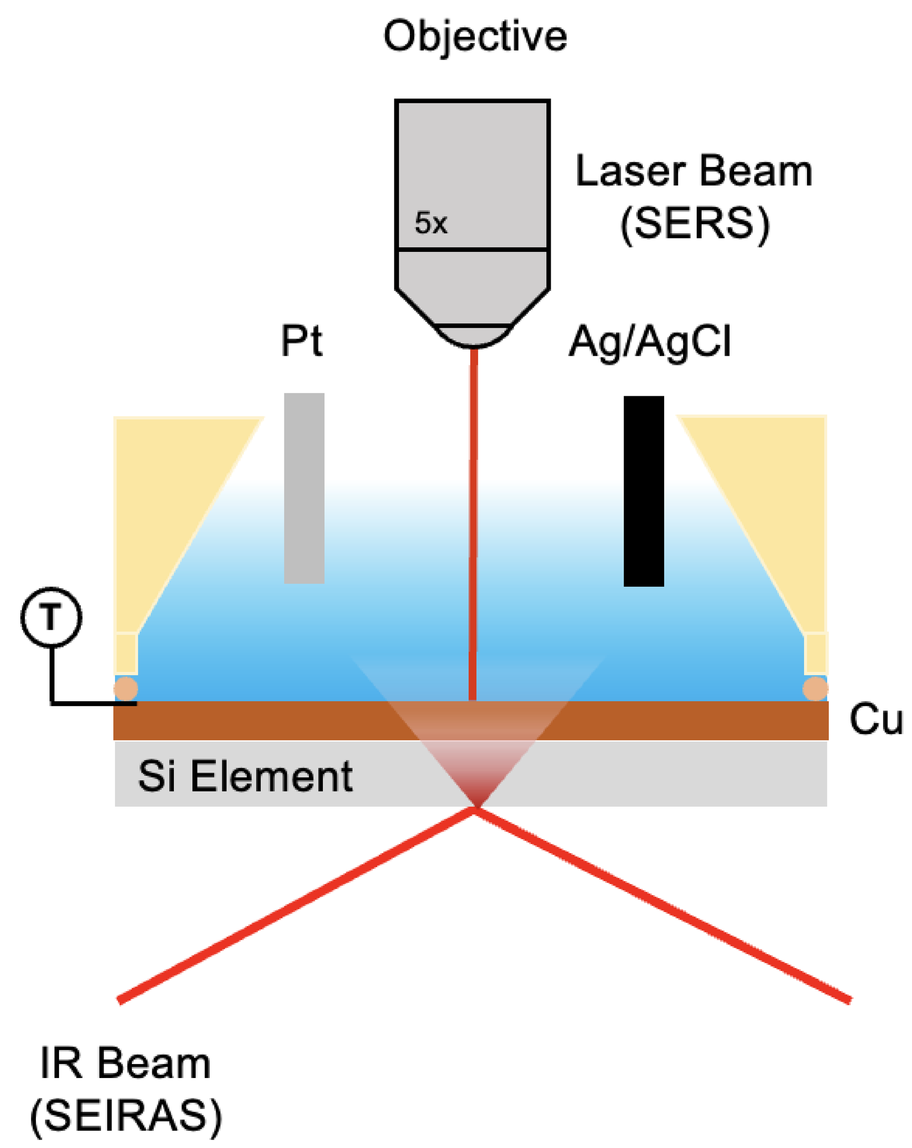
- There has been a growing interest to decarbonize the chemical industry to meet net zero emission goals by 2050.[1]
- Electrochemical conversion of carbon dioxide (CO_2RR) stands out as a pathway to mitigate carbon emissions and convert CO_2 to valuable multi-carbon products.[2]



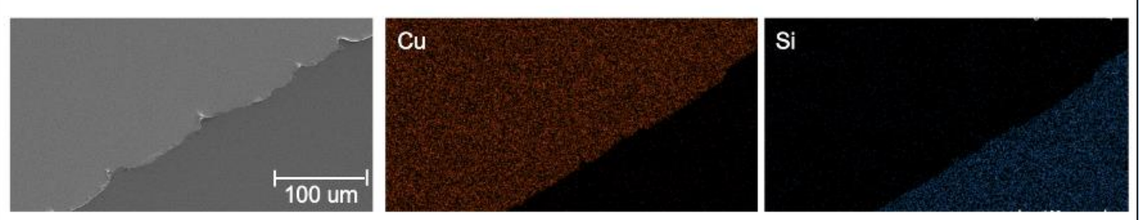
- Copper is the only pure metal that can efficiently convert CO_2 to multi-carbon products, but its selectivity is highly dependent on the local microenvironment.[2]
- To be competitive with existing chemicals manufacturing, the selectivity to multi-carbon products and the process energy efficiency need to be improved.
- **Objective:** this work aims to make this reaction more sustainable by engineering the reaction microenvironment to enhance ethylene selectivity and reduce process energy requirements.
- **How:** to engineer the reaction microenvironment, we combine product analysis with in-situ spectroscopic techniques to track how intermediates convert and products form under different operating conditions.

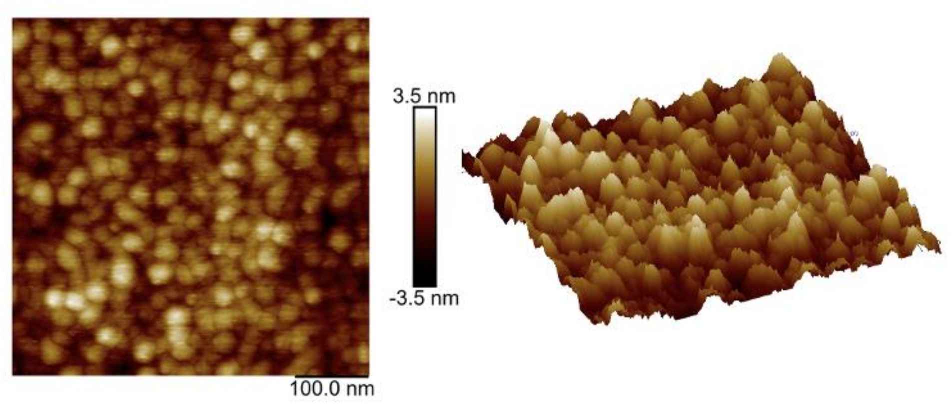
Methods Used

- Two spectroelectrochemical reactors were built to electrolyze Ar-purged, CO_2-saturated $KHCO_3$ electrolytes.
- Reactors allow spectroscopic information collection (surface-enhanced infrared and Raman) and gas and liquid product analysis (μ-GC and HPLC).



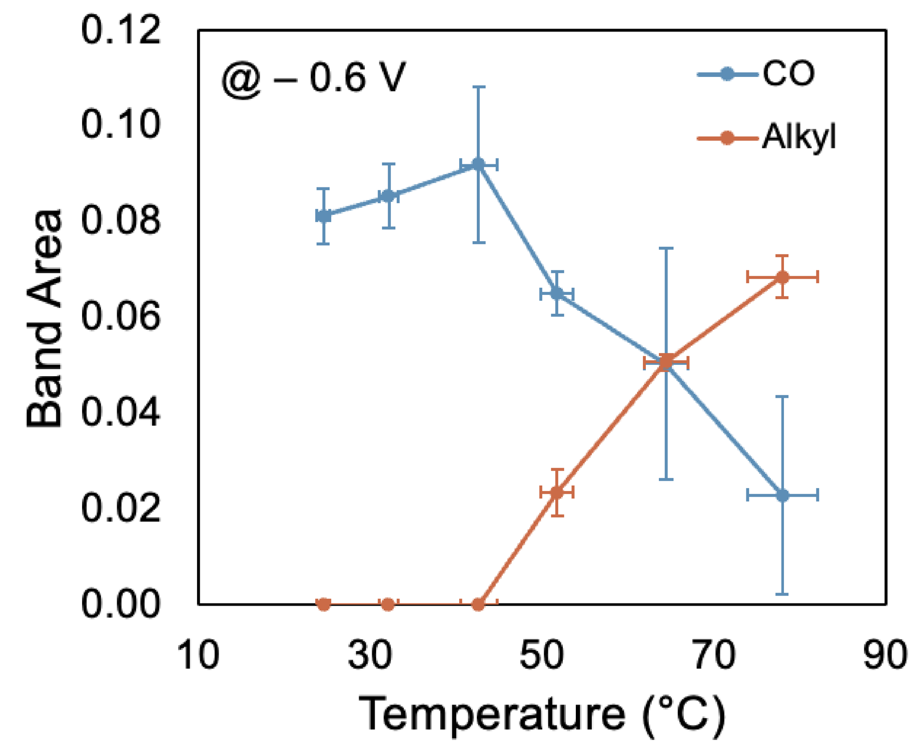
- Different potentials (0.1 to – 0.6 V vs. RHE), temperatures (25 to 75 °C) and electrolyte media can be modulated.
- Copper catalysts are synthesized, characterized and pre-treated through different routes to test multiple reaction engineering strategies.



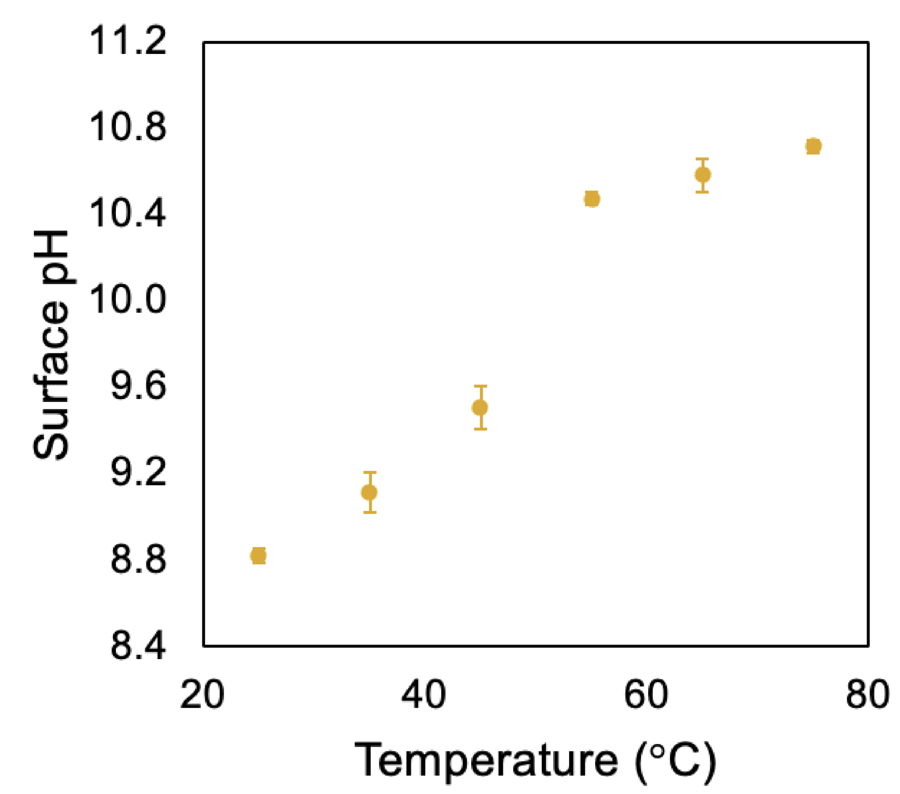


Results and Discussion

- CO is a common intermediate in the reduction of CO_2 to C_1 and C_2 products.
- SEIRAS revealed that site-specific CO coverage is dependent on temperature, and that CO migration directly impacts ethylene formation at higher temperatures.
- Increasing temperature led to decreased CO and increased alkyl groups coverage for a given potential.

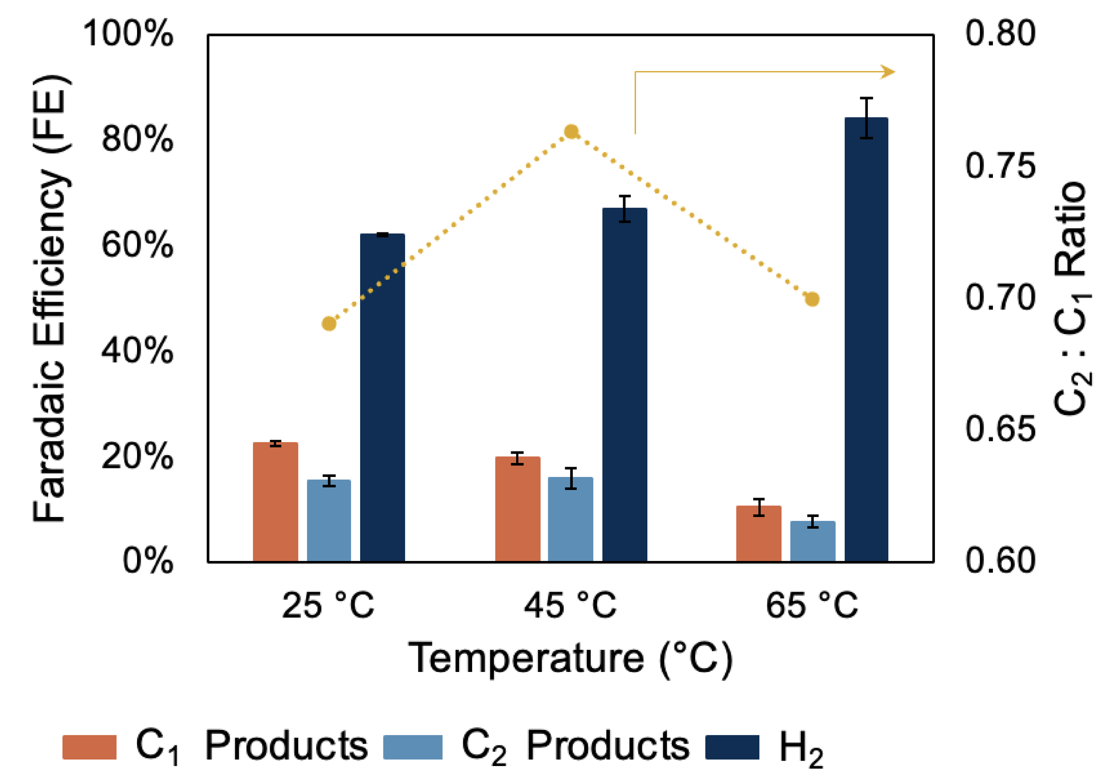


- Temperature has a direct effect on the selection of mechanistic pathways in the conversion of CO_2 to C_1 and C_2 products.
- SERS revealed that surface pH is considerably higher than bulk pH, and higher temperatures led to higher surface pH values.



Results and Discussion

- Significant depletion of local hydrogen with increasing temperature indicates that local pH plays a key role in driving reaction selectivity dependence on temperature.
- Maximum in multi-carbon products selectivity was observed between 45 and 55 °C.



Conclusions

- Temperature is a microenvironment parameter that dramatically affects reaction surface dynamics and product formation.
- Microscopic understanding of the effect of these parameters on the reaction is a key step to rationalize product distribution and scale up of practical CO_2 electrolyzers.
- Sustainable design of CO_2 electrolyzers relies on similar reaction engineering strategies to target multi-carbon products formation.

References

1.arXiv (Cornell), 2023, 2305.05165
2.J. Am. Chem. Soc. 2022, 144, 33, 15047–15058
3.Electrochem. Eng. Lab at Sydney. 2024, NSW 2006