

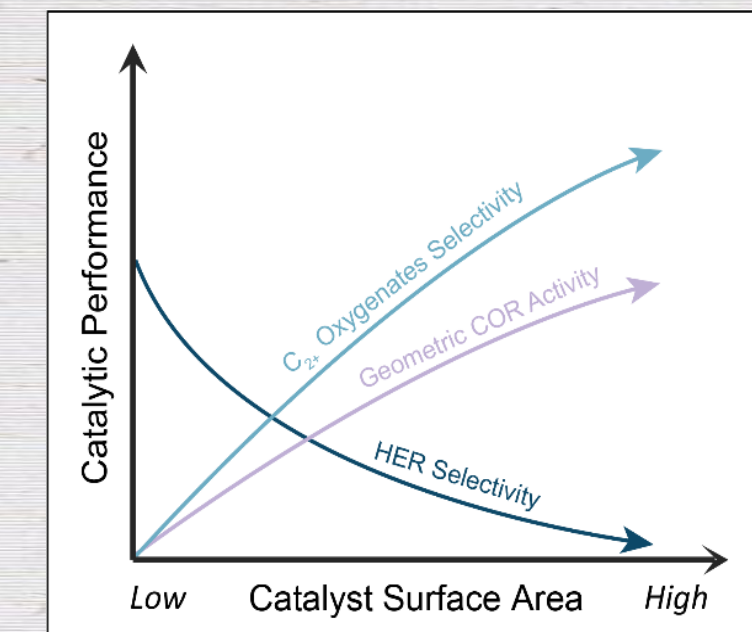
CO and CO₂ Reduction on Copper Electrocatalysts: Controlling Selectivity to Oxygenated and Multi-Carbon Products

Lei Wang, Stephanie Nitopi, Xinyan Liu, Daniel Corral, Karen Chan, Jens K. Nørskov, Christopher Hahn, and Thomas F. Jaramillo

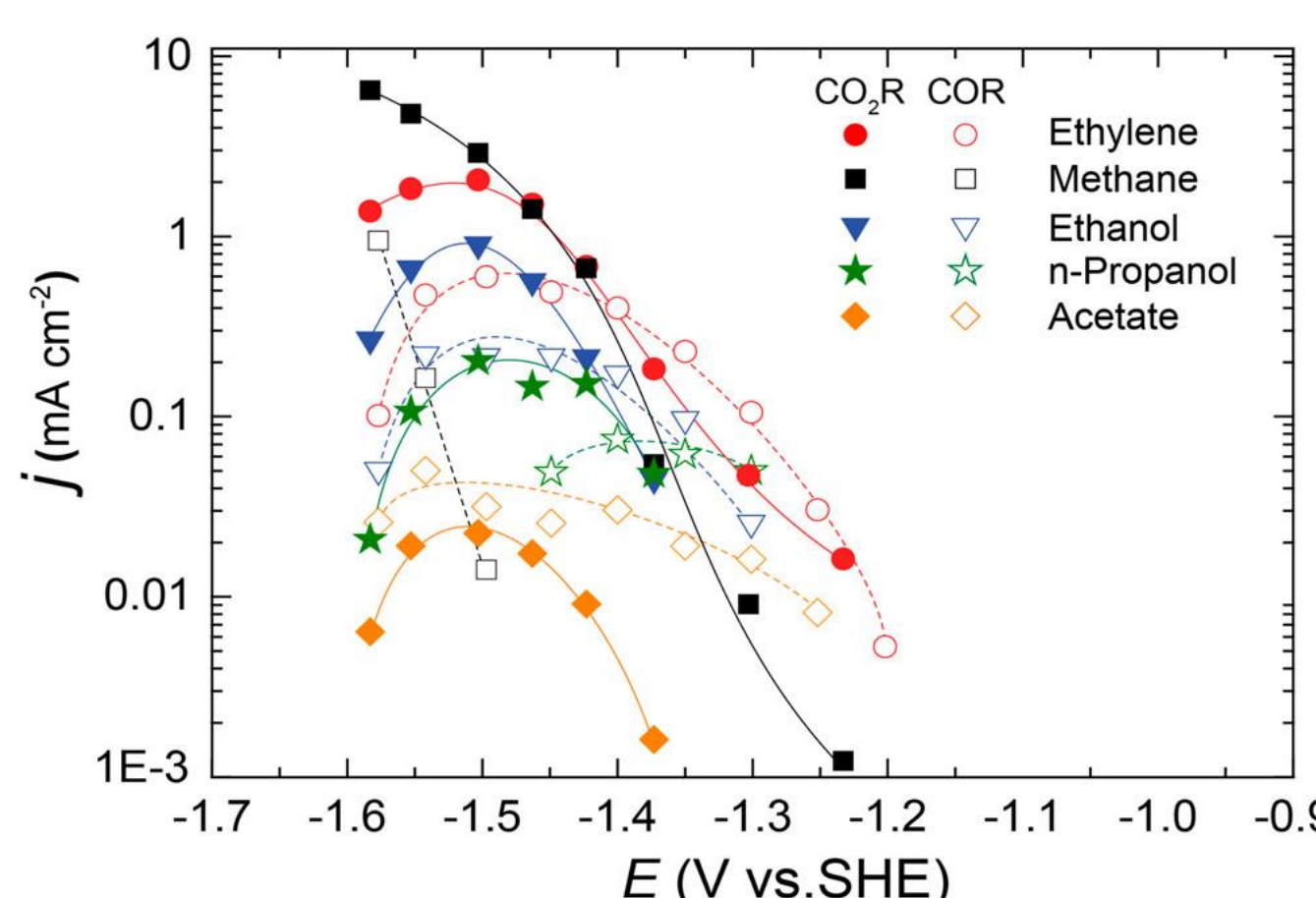
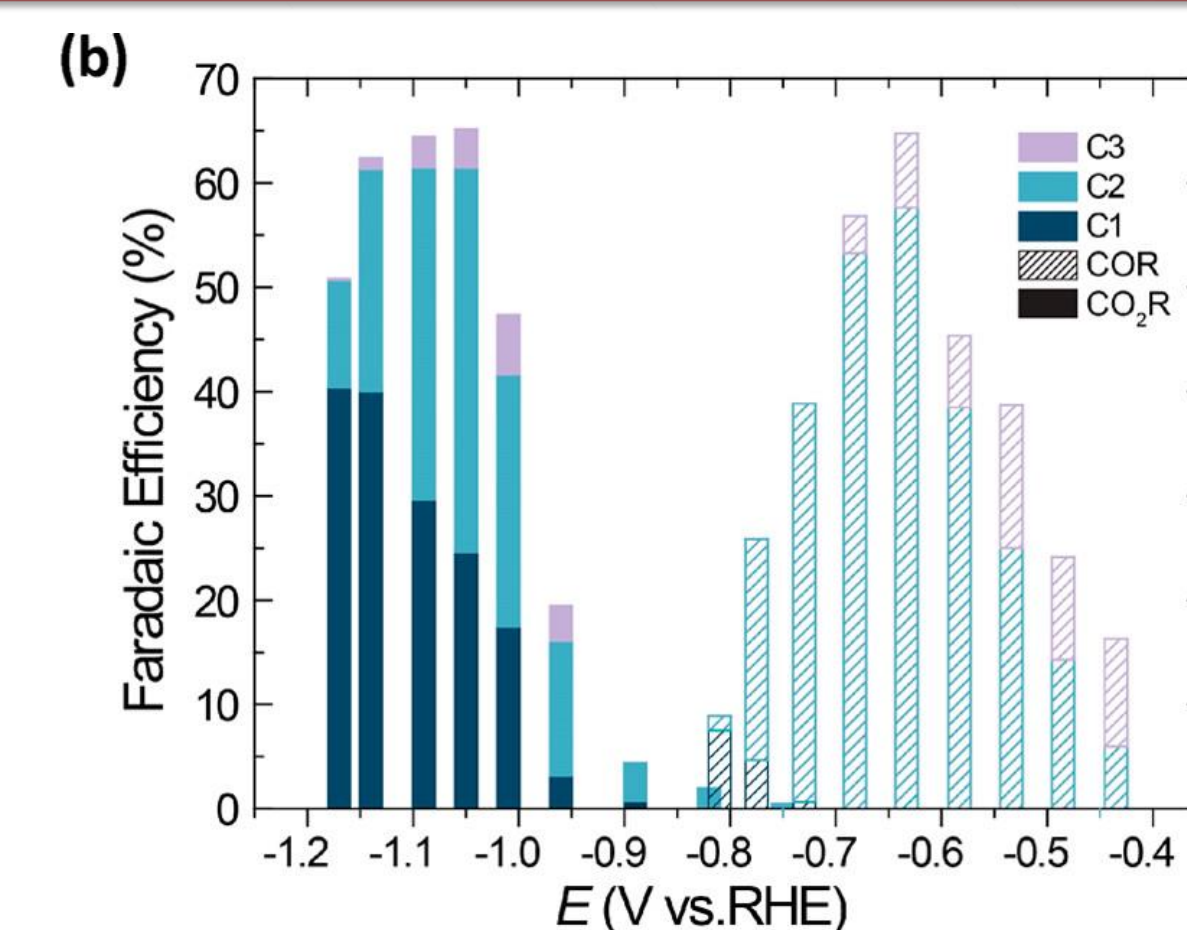
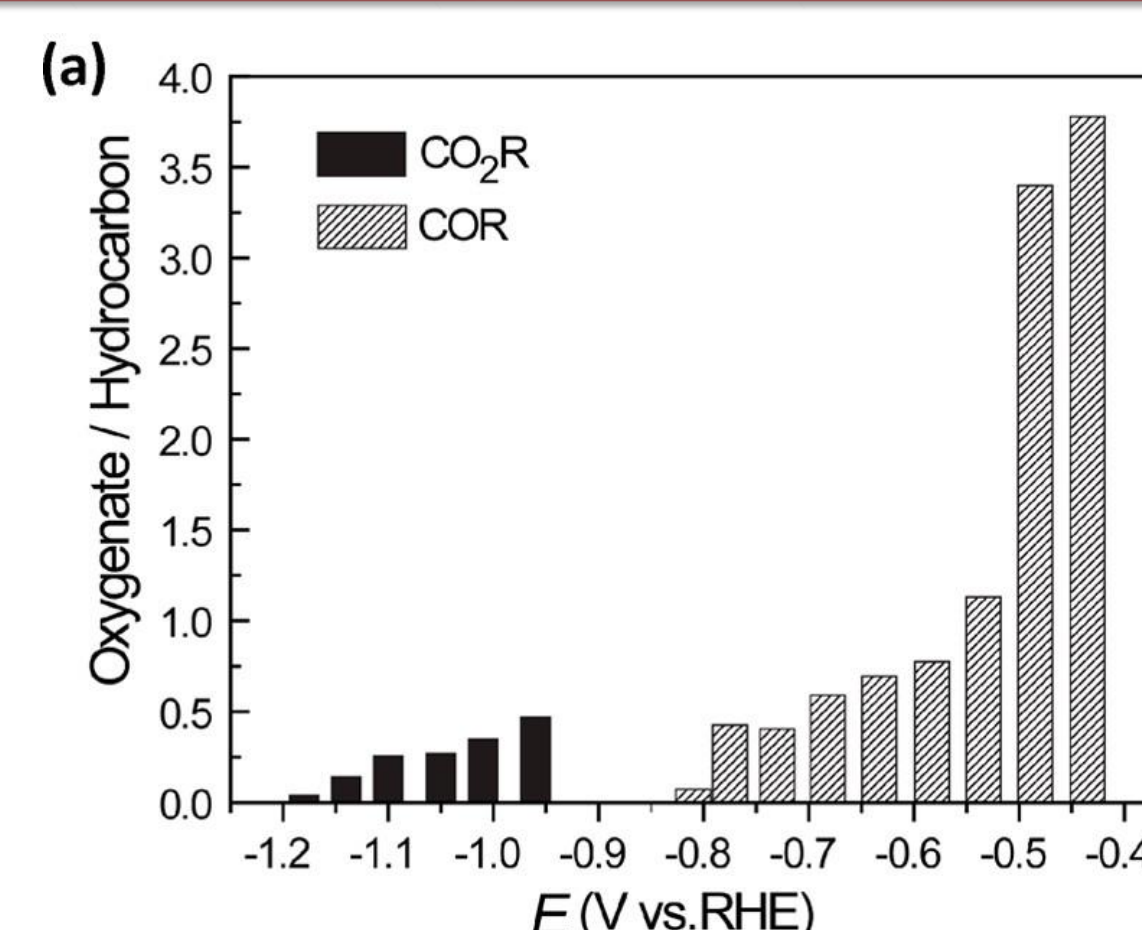
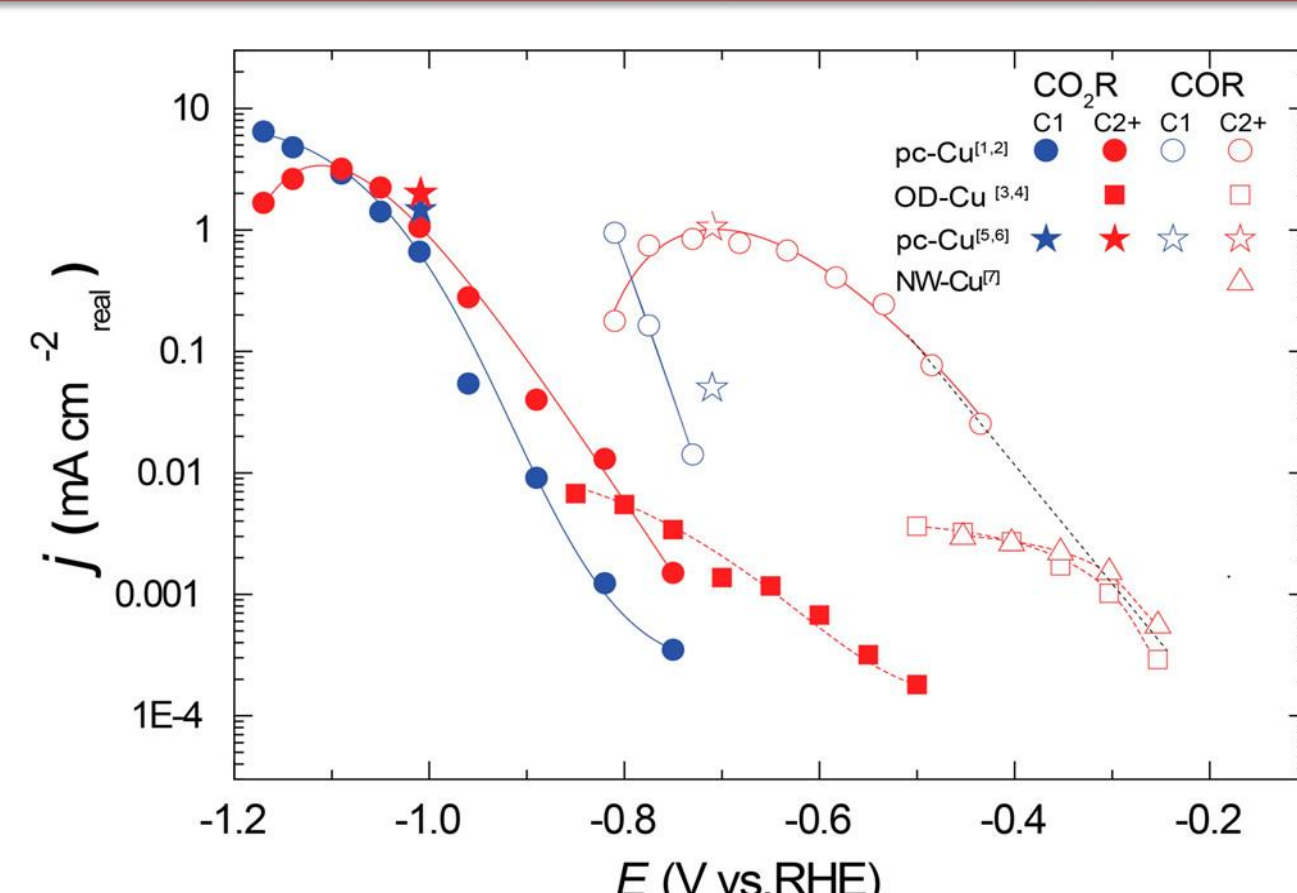
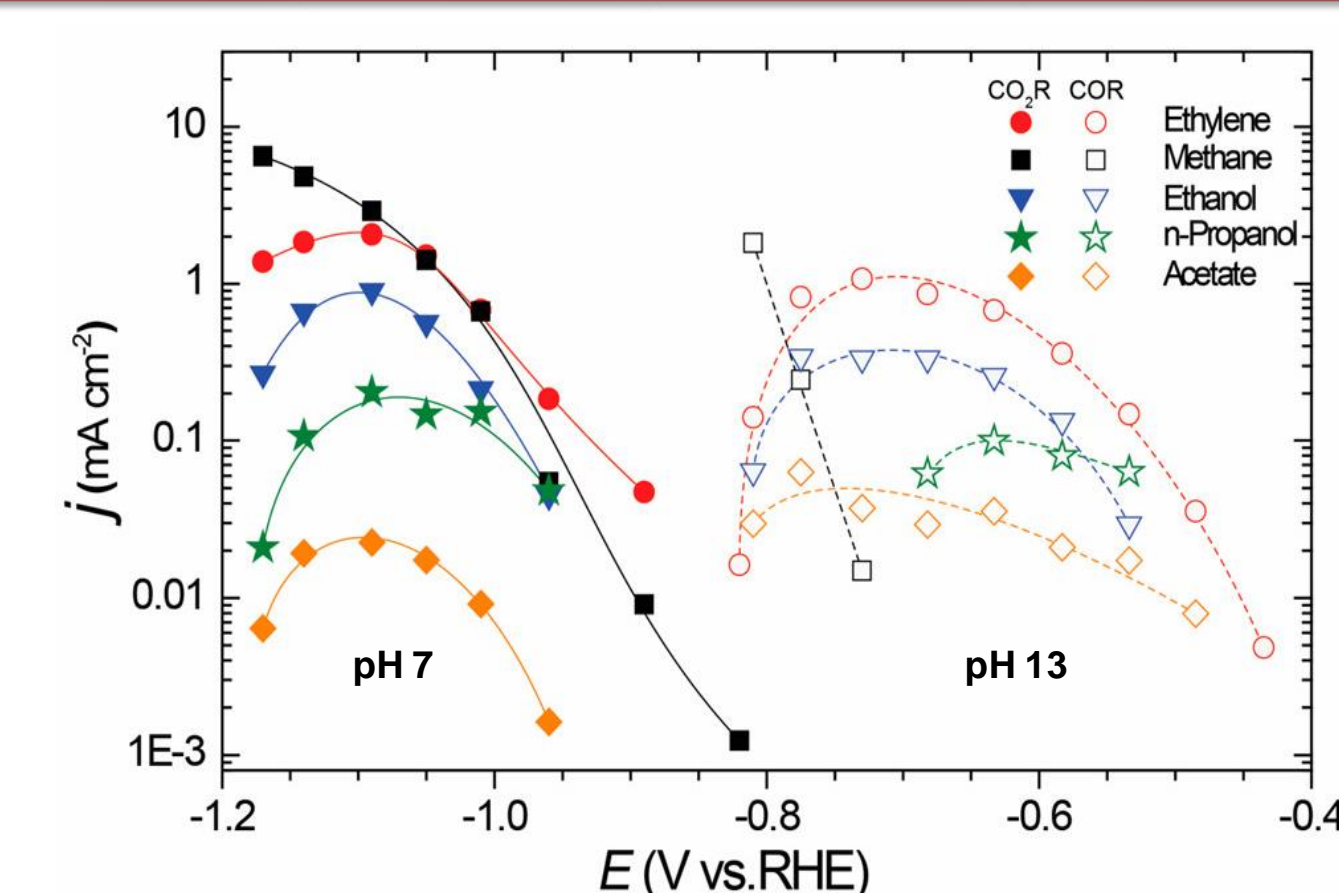
Summary

In this work, both low and high surface area polycrystalline Cu (pc-Cu) are investigated for CO reduction (COR) under alkaline conditions and CO₂ reduction (CO₂R) under neutral conditions. There is a large positive shift in the overpotential for C–C coupled products under CO reduction conditions, which we conclude is primarily the result of a pH effect. Further analysis of the reaction products reveals common trends in selectivity that indicate both the production of oxygenates and longer carbon chains are favored at lower overpotentials. These selectivity trends are generalized by comparing the results on planar Cu to high surface area Cu catalysts, such as our novel Cu flower nanomaterial, which are able to achieve high oxygenate selectivity by operating at the same geometric current density at lower overpotentials. Combined, these findings outline key principles for designing CO and CO₂ electrolyzers that are able to produce valuable liquid products with high energy efficiency.

Catalyst Design Principles

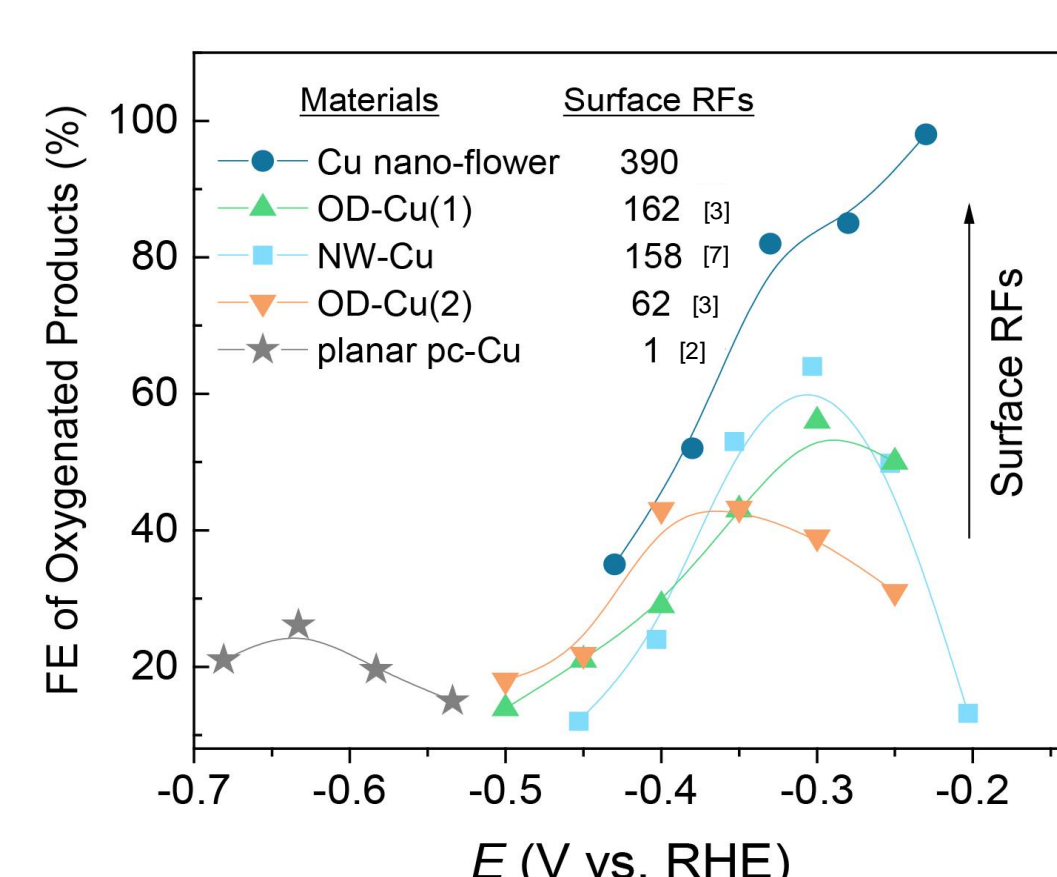
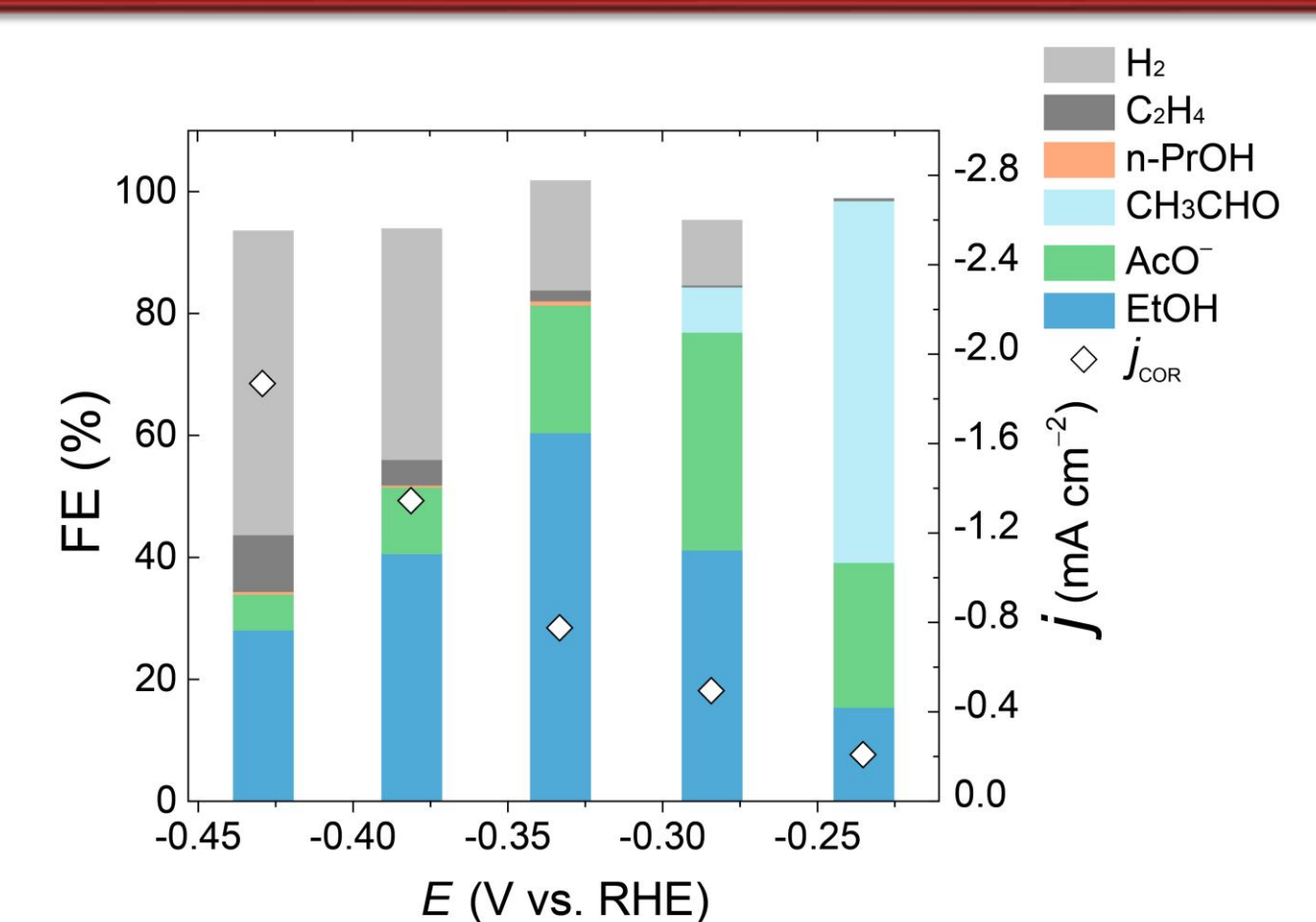


Activity and selectivity trends for planar pc-Cu for COR and comparison to CO₂R

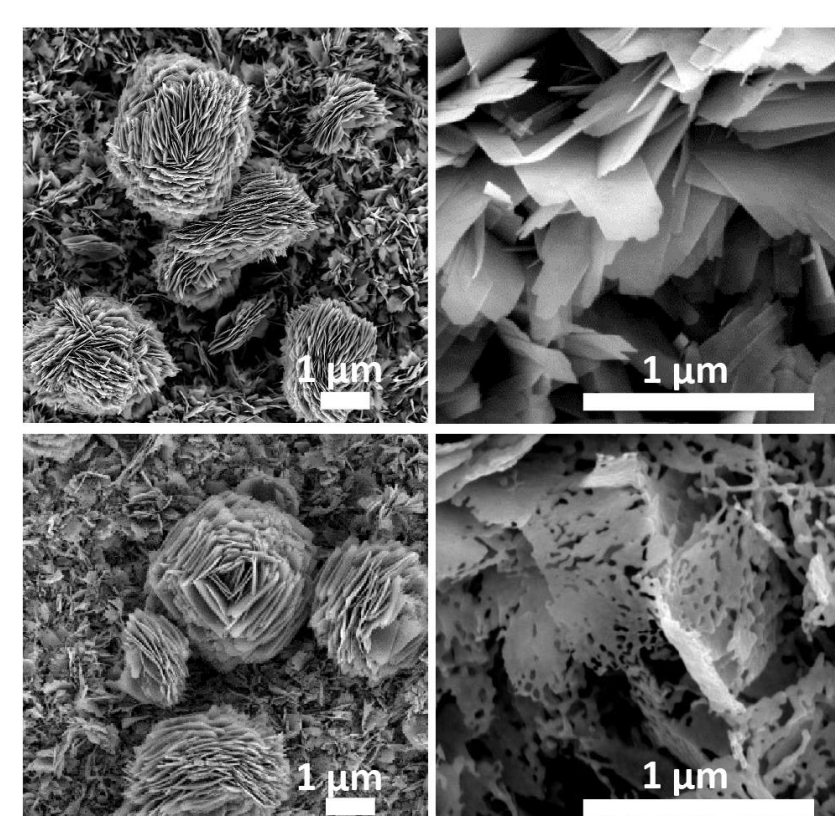
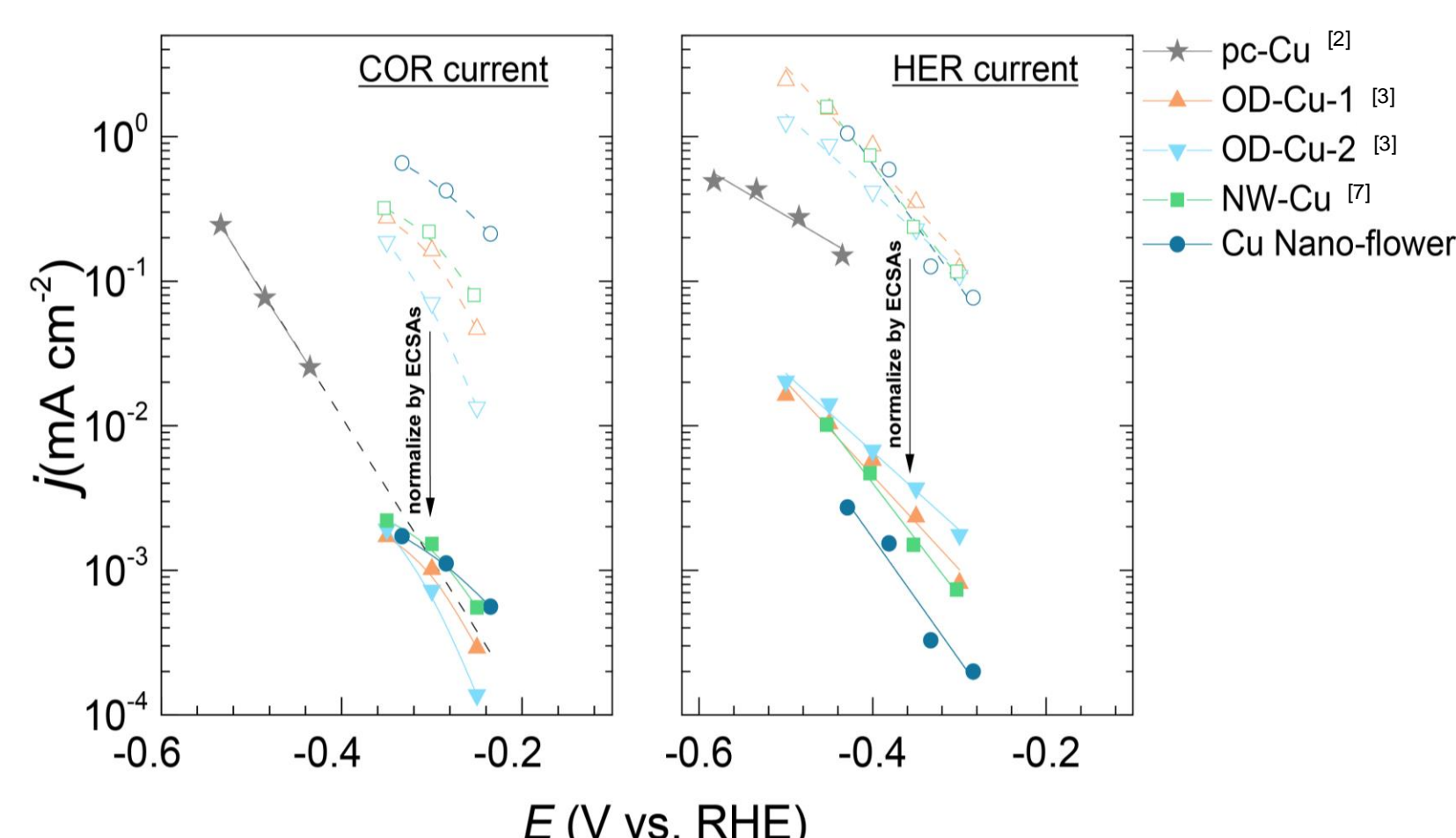


- Seven major COR products were observed, which are also common to CO₂R, strongly indicating that CO is a key reaction intermediate for these products.
- There is a large positive shift in overpotential for C–C coupled products under COR conditions.
- The effects of CO partial pressure and electrolyte pH were investigated; we conclude that this is primarily a pH effect.
 - Theoretical understanding: C₁ has later RDS and therefore higher Tafel slope and mixed RHE/SHE dependence; C₂₊ has earlier RDS and therefore a smaller Tafel slope and pure SHE dependence.
- Alkaline conditions can thus improve the energy efficiency and selectivity towards C₂₊ products.
- Both the production of oxygenates (a) and the growth of longer carbon chains (b) are favored at lower overpotentials.
- The selectivity difference between high surface area and planar pc-Cu is likely due to operation under different applied potentials.

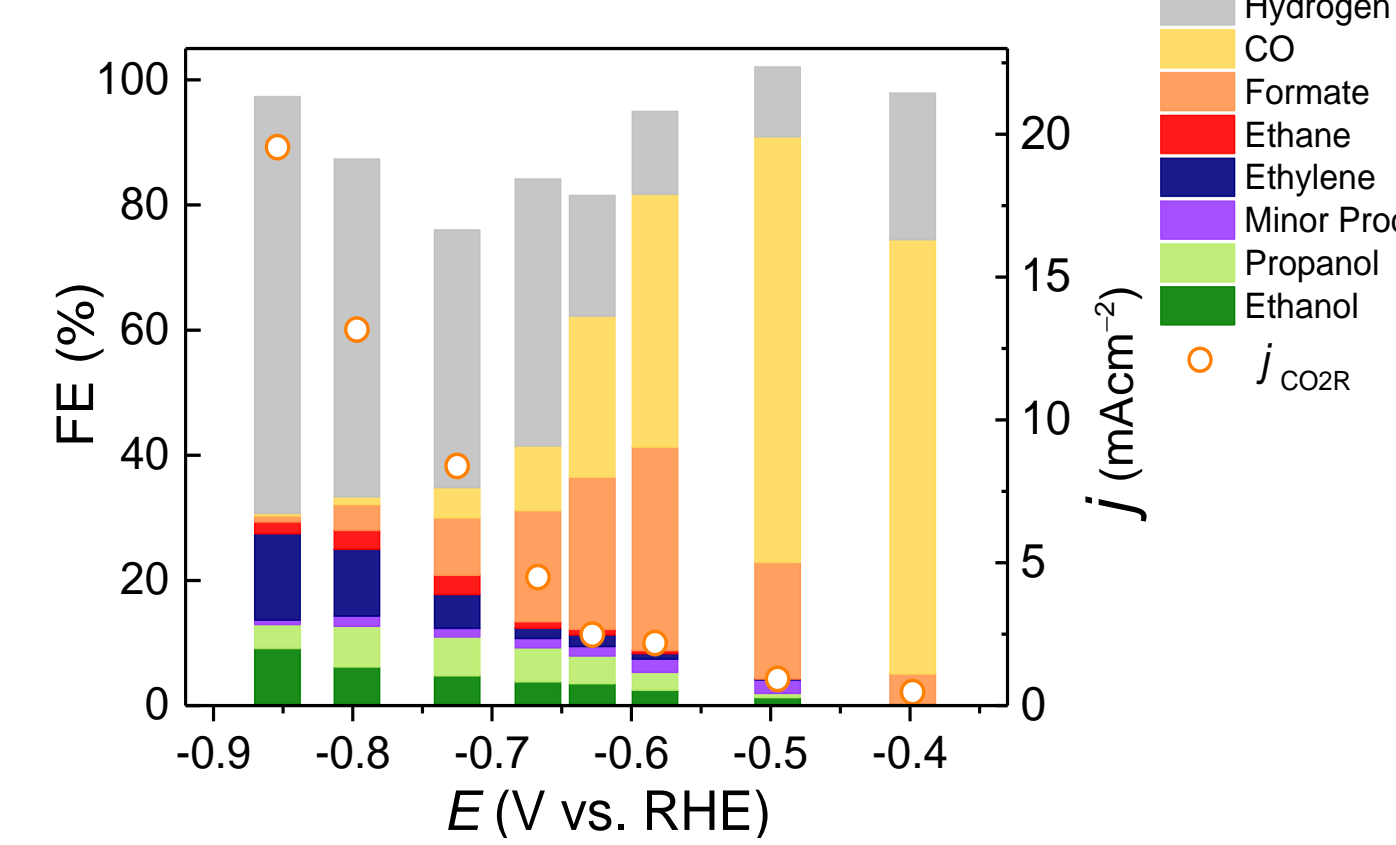
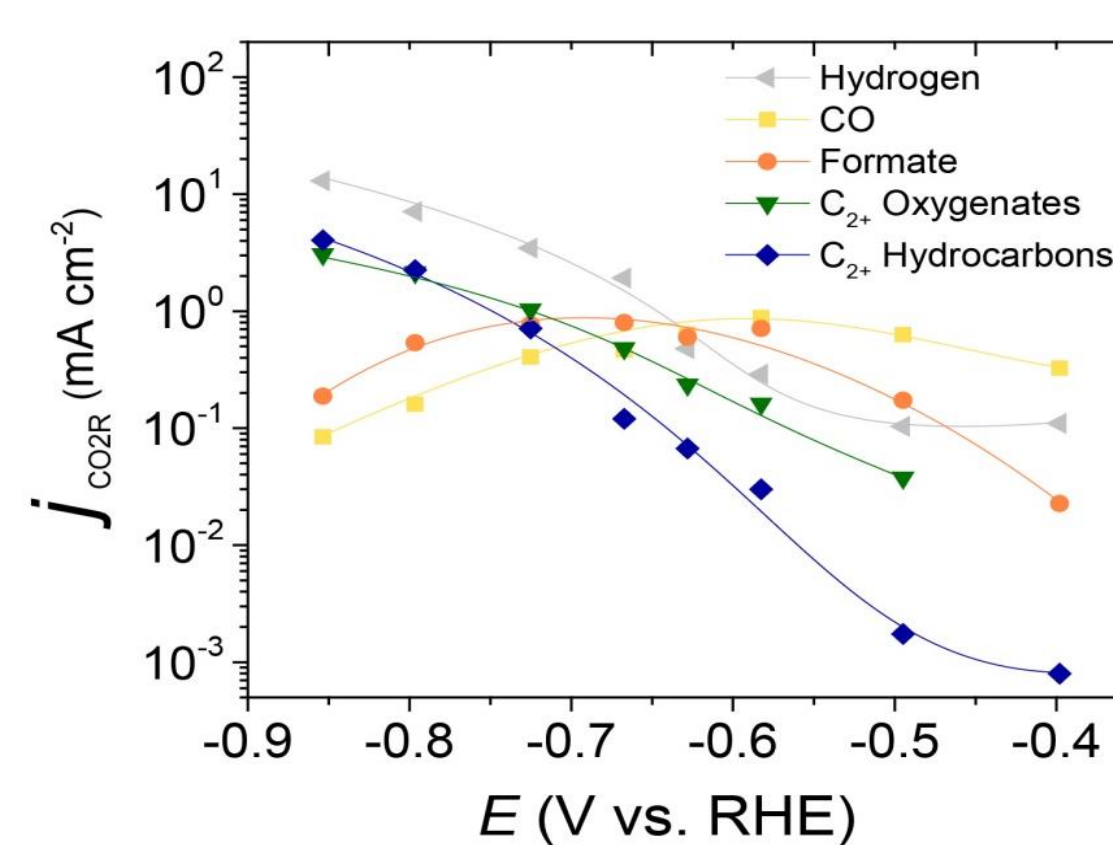
COR on high surface area pc-Cu flowers



- High selectivity to liquid products achieved at low overpotentials.
 - ~100% selectivity for COR to C₂₊ oxygenates at -0.23 V vs. RHE
- C₂₊ oxygenates production scales with the surface roughness factors (RFs).
- Current densities normalized by the electrochemically active surface area (ECSA) for planar and high surface area Cu show comparable intrinsic activities for COR; HER rates, however, appear to be suppressed on rougher Cu materials.



CO₂R on high surface area pc-Cu flowers



- CH₄ pathway is completely suppressed.
- At low overpotentials, 2e⁻ products CO and HCOO⁻ are favored.
- At high overpotentials, C₂₊ products are favored.
 - >30% FE and ~6 mA/cm² observed for C₂₊ products
- Oxygenates are favored at lower overpotentials compared to hydrocarbons.
- Physical characterization of the Cu nano-flowers pre-test (top) and post-test (bottom) suggests that the material is pc-Cu and remains stable during catalysis.

References

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