Electrode Potential, pH and Bimetallic effects on Selectivity of Electrochemical Carbon Monoxide Reduction

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Introduction

In this work, low and high surface area polycrystalline Cu (pc-Cu), and bimetallic CuAg electrodes are investigated for carbon monoxide reduction (COR) under alkaline conditions. By comparing the CO2R on pc-Cu at pH 7 to the COR on pc-Cu at pH 13, it is clear that 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.

CuAg bimetallic electrodes have been investigated for CO reduction under alkaline conditions. Unprecedented selectivity to acetaldehyde was obtained at low overpotentials on planar CuAg electrodes. DFT calculations demonstrate that the Ag ad-atoms can tune the surface binding energy of reduced aldehyde intermediates, resulting in a suppression of acetaldehyde reduction to ethanol.

Combined, these findings outline key principles for designing CO and CO2 electrolyzers that are able to produce valuable liquid products with high energy efficiency.

Outlook

- Future work on exploring the mechanism of HER suppression can lead to the design of new and active and hihgly selective electrocatalysts for CO2R and COR.
- Future work will incorporate high surface area Cu into a gas diffusion electrode (GDE) device to achieve better mass transport and further the design of practical CO2R/COR electrolyzers.

Acknowledgments

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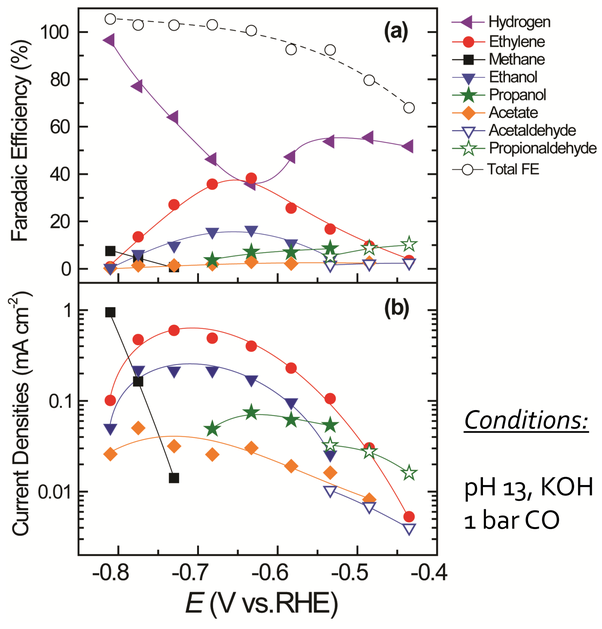
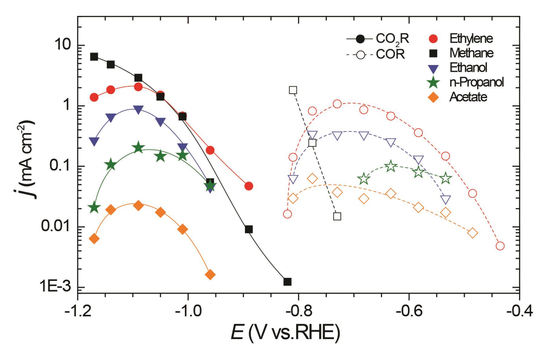
Results, Highlights, and Conclusions

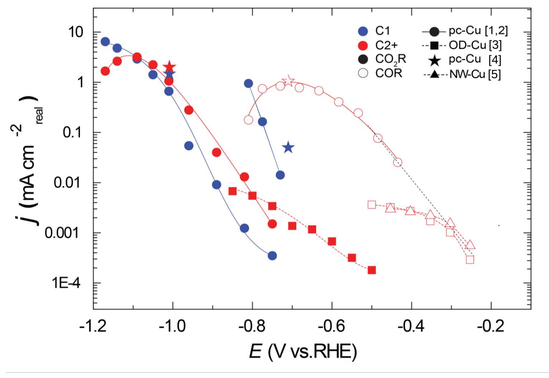
Activity and selectivity trends for planar, pc-Cu for COR and comparison to CO2R

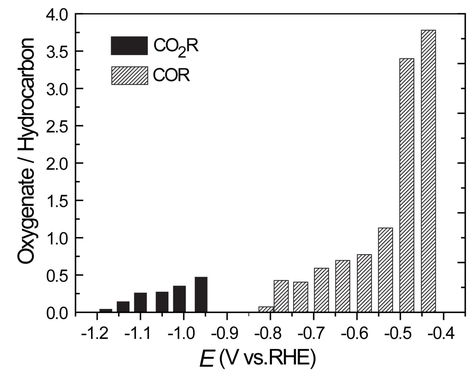


Conditions:

pH 13, KOH
1 bar CO



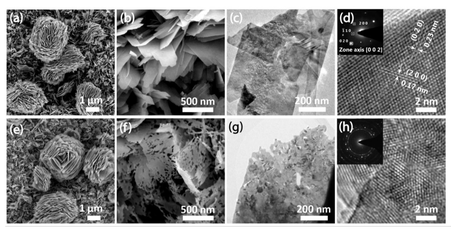




- Seven major COR products were observed which are also common to CO_2R, strongly indicating that CO is a key reaction intermediate for these products.
- There is a large positive shift in overpotential for C–C coupled products under COR conditions.
- The effects of CO partial pressure and electrolyte pH were investigated; we conclude that this is primarily a pH effect.
- Both the production of oxygenates and the growth of longer carbon chains are favored at lower overpotentials.
- Selectivity difference between high surface area and planar pc-Cu is likely due to operation under different applied potentials.

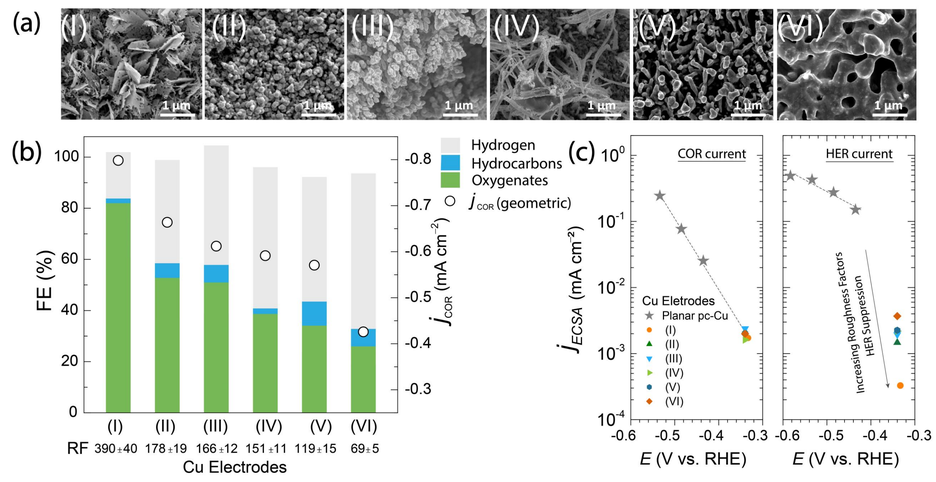
COR on high surface area Cu flowers

SEM and TEM images of the Cu flower materials

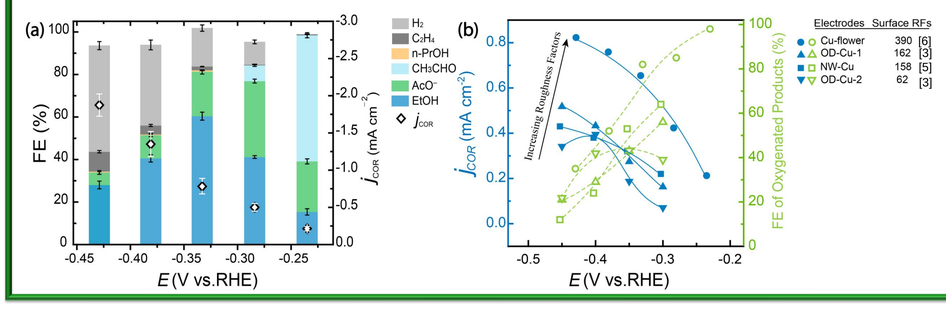


- Physical characterizations suggest that the CuO flakes are the precursor of the Cu flower.
- The Cu flower is obtained by electrochemical reduction of the CuO precursor under the catalytic conditions.
- HR-TEM suggests that the Cu flower is in polycrystalline form, no evidence of special active sites formation.

COR on Cu-based electrodes with different surface area



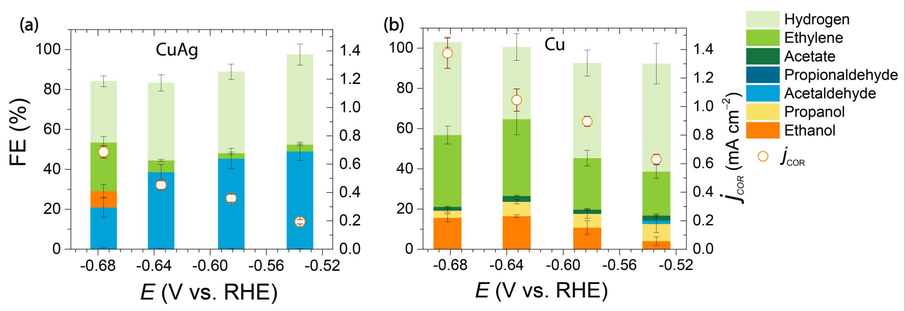
COR on Cu flower and comparisons to other high surface area Cu-based electrodes



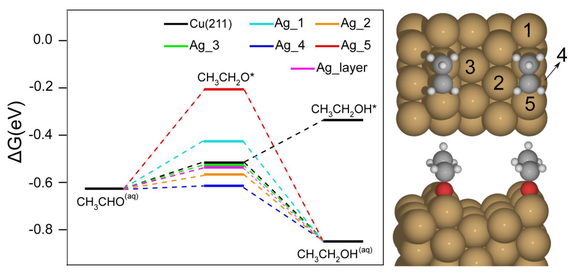
- High selectivity to liquid products achieved at low overpotentials.
- Current densities normalized by the RF for planar and high surface area Cu show comparable intrinsic activities.

COR on CuAg bimetallic electrode

COR comparisons on planar Cu and CuAg under the same conditions, pH 13 [7]



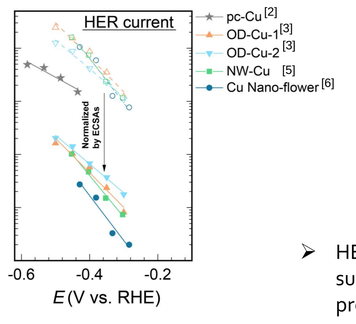
Theoretical understanding of the bimetallic effect



- High selectivity towards acetaldehyde was obtained on planar CuAg electrodes at low overpotentials , which is attributed to the bimetallic effect: Ag ad-atoms can tune the surface binding energy of reduced aldehyde intermediates.

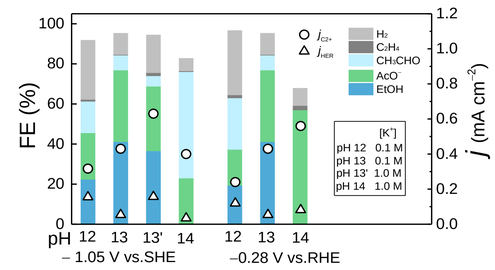
HER suppression on high surface area electrodes

The competing reaction HER on different Cu-based electrodes



Conditions:
pH 13, KOH, 1 bar CO

CVs and Tafel plots planar Cu and Cu flower under nitrogen



- HER is suppressed on high surface area Cu electrodes is suppressed, this contributes to the high selectivity of liquid products for COR.
- Similar HER suppression is observed in absence of CO.
- The suppression is not directly link to the high pH environment.

References

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