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Investigating the Impact of Strain on Electrochemical CO2 Reduction Using Model Bulk Metallic Glass Materials
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In the 2nd year of our project, we achieved record production of ethanol and propanol and sizable acetate production from CO_2 electrolysis using a mesostructured copper catalyst, a result now published in *ACS Applied Energy Materials*.[*] We also have gained early results toward fundamental insight into the role of strain in controlling critical adsorbate binding energy using model materials. We summarize the two advances below.

1. Mesostructured Copper electrocatalyst

The electrocatalytic selectivity for CO_2 reduction products of operando Cu catalyst prepared from $Cu(OH)_2$ nanowire precursors is strongly governed by a potential-dependent mesostructure. Tuning the morphology generates catalysts with enhanced Faradaic efficiency (FE) for valuable C_2-C_3 compounds as shown in Figure As shown in Figure 1a, $Cu(OH)_2$ nanowire precursors turn to mesostructured morphologies with respect to the applied potential. Total FE for C_2−C_3 products maximized (~38%) at moderate potentials (−0.81 V RHE) as shown in Figure 1b. mesostructured Cu catalyst tunes selectivity from C_0-C_1 compounds to highly reduced compounds relative to planar Cu electrodes. This is attributed to formation of a hierarchical nanorod/nanoparticle morphology that induces

Figure 1. The effect of catalyst morphology on CO_2 reduction products selectivity. (a) SEM images of catalyst after electrolysis for (i) 60 min at -0.81 V vs RHE, (ii) 10 min at -1.08 V vs RHE and 50 min at -0.81 V vs RHE, and (iii) 60 min at -1.08 V vs RHE. (b) FE of C_2-C_3 compounds with respect to the applied potential.

an effective microreactor environment for forming C_2−C_3 compounds. Furthermore, the catalysts maintain the performance for 40 h of CO_2 electrolysis, indicating stable catalysis.[*]

Insights: These findings demonstrate that the enhanced selectivity of CO_2 reduction reaction (CO2RR) to C_2−C_3 compounds and especially alcohols at moderate overpotentials using a mesostructured Cu catalyst can be attributed to the formation of a favorable, potential- dependent morphology. This structure may results from the volume change during the in situ reduction from $Cu(OH)_2$ nanowires to produce the catalyst that has significant surface strains and likely generates active defect sites.[1] Further study is required to fully attribute the effect of surface strains and resulting active defect sites on enhanced CO2RR product selectivity. Demonstrating the CO2RR reaction mechanisms coupled with key intermediates (e.g. *CO, *OCHO, *HCO, and *CHO) with the magnitude of applied strain on the catalyst surface will highlight the potential opportunity to create active and selective electrocatalyst for difficult multielectron reactions.

2. Strain-induced Electrochemical CO2RR using polycrystalline planar Cu electrode

Strain is known to play a key role in determining the binding energy of adsorbates in canonical electrochemical reactions such as hydrogen evolution and oxygen reduction. Little is known regarding the effects on CO_2 electrolysis. We examined the FE of polycrystalline planar Cu as a function of tensile stain at varying potentials. In the low overpotential range (< -0.9 V vs RHE), H_2, CO, and formate are mainly observed, suggesting insufficient overpotential to produce more reduced products. At -0.9 V vs RHE, FE of CO shows a gradual increase (from 36% to 57%) within elastic strain regime (< 0.15%), while significant decrease in that of CO is observed in the plastic strain regime. On the other hand, FE of formate shows plateau (~ 4%) from 0% to 0.18% of strain, and it surpasses 18% at 0.24% of strain. This may indicate that the tensile strain strongly affects *CO binding energy, especially in
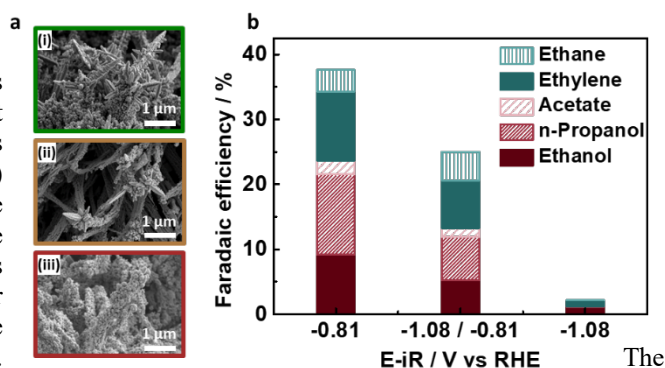
[*] T. Kim, A. Kargar, Y. Luo, R. Mohammed, E. Martinez Loran, P. Shah, D. P. Fenning*, "Enhancing C2-C3 Production from CO2 on Copper Electrocatalysts via a Potential-Dependent Mesostructure," ACS Applied Energy Materials,1 (5), 1965-1972, 2018.

the plastic regime, and formate formation occurs along with an independent reaction pathway.[2–6] CH_4, a more reduced product, is observed as one major product in higher overpotential range (> -1.1 V vs RHE). The Cu electrode shows opposite trends of FEs for CO and CH_4 with respect to strain, suggesting that tensile strain tunes binding energy of *CO, a key intermediate. In elastic strain regime (< 0.15%), FE of CO increases from 7% to 37%, while that of CH_4 suppressed from 34% to 1% at -1.1 V vs RHE. In plastic strain regime (> 0.15% and < 0.3%), FE of CH_4 increases to 35%, while that of CO decrease to 3%. This is probably due to onset of plasticity that induces defect formation at the planar Cu surface. Interestingly, FE of H_2 shows rather plateau with respect to the strain, indicating tensile strain has no critical influence on proton-coupled electron transfer reaction.

Partial current density of CO (j_{CO}) plateaus throughout the strain regime at -0.7 V vs RHE, while that of formate ($j_{formate}$) shows concave down behavior in the elastic strain regime. J_{CO} surpasses the partial current density of H_2 (j_{H2}) at 0.15% of strain and decreases in the plastic regime at -0.9 V vs RHE. Formate production increases with strain as CO production decreases, indicating a possible tradeoff between the binding of key intermediate of formate (*OCHO) and *CO as a function of strain. At higher overpotential (> -1.1 V vs RHE), increase in partial current density of CH_4 (j_{CH4}) occurs where j_{CO} starts plateaued (from 0.11% to 0.18% of strain). This indicates the surface coverage of *CO is highly related on the CO_2RR[7] and it can be tuned by tensile strain. The j_{H2} and j_{CH4} inclines beyond the elastic strain regime, suggesting highly favored proton-coupled electron transfer reaction. The partial current density of EtOH (j_{EtOH}) also increases where j_{CO} starts plateaued, suggesting that CH_4 and EtOH formation may occur through a similar reaction pathway via a *CO intermediate.[6]

Insights and plans: The work herein demonstrate that tensile strain can manipulate selectivity of CO_2RR products with respect to its applied magnitude. At low strains <= 0.1%, we see that the FE of CO increases with respect to strain while that of CH_4 is suppressed at -1.1 V vs RHE, indicating a decrease in binding energy of *CO and a favoring of CO leaving the surface. With higher magnitude of strain (> 0.15%), FE of CH_4 rises and that of CO decreases that suggests the binding energy and surface coverage of *CO increase when moving from the elastic to plastic regime.[7]

We plan to examine single crystal surfaces and use computational and theoretical studies such as DFT and microkinetic modeling studies are also necessary to support the idea that strain engineering is a tunable approach to modifying the surface binding energy of CO_2 reduction intermediates and crystalline structure, resulting in designing a selective electrocatalyst.

3. Impact on Students participating and on my Career

The ACS PRF DNI support has been instrumental in the training of Ph.D. candidate Taewoo Kim. He has spent two years focused on the project, gaining valuable expertise and depth in heterogeneous catalysis and electrocatalysis. This will serve him well in his future pursuits beyond graduate school either in industry, including in the petroleum industry, or in academia. ACS PRF support enabled me to establish a foundation as a new investigator in the CO_2RR. Building the *in situ* strain-catalysis cell has provided me with a unique tool and lens to investigate important heterogeneous catalysis reactions for my career. We have now established a publication record, which will continue to grow after the active project period ends based on ACS PRF support. We will continue to gratefully acknowledge the PRF support.

4. References

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