Abstract:

Global dependence on fossil fuels as energy sources and the alarming increase of greenhouse gas emissions has necessitated the development of carbon-free and carbon-neutral renewable energy sources for the future. The sequestration of CO₂ emissions along with subsequent electrochemical reduction into fuel products, forms a carbon-neutral synthetic fuel cycle which could potentially be streamlined into existing fuel infrastructures. To date, only Cu has displayed any propensity as a catalyst to electrochemically reduce CO₂ into longer chain hydrocarbons. Previous studies on Cu single crystals have shown large facet sensitivities for electrochemical CO₂ reduction product selectivity. The aim of our research is to utilize these surface structure motifs to design active and selective catalysts that are amenable to device integration. Here, we discuss our recent progress with the epitaxial growth of Cu thin films in both low and high Miller index orientations for electrochemical CO₂ reduction.

Introduction

Epitaxial Growth of Cu

(A) Symmetrical XRD scans demonstrate that different orientations of Cu can be grown by utilizing the interfacial energy of a single crystal substrate. (B) Symmetrical XRD scans probe scattering vectors normal to the substrate.

Research Plans

- Utilize physical vapor deposition to epitaxially grow Cu thin films on single crystal substrates.
- Confirm epitaxial growth using a combination of X-ray diffraction (XRD) scans to probe out-of-plane and in-plane thin film texture.
- Test the electrochemical CO₂ reduction activity and selectivity of epitaxially grown Cu thin films.
- Analyze/quantify the gas and liquid phase product distribution using gas chromatography (GC) and nuclear magnetic resonance (NMR), respectively.
- Interface with other JCAP materials discovery projects to utilize the insights gained from these studies to design active and selective bimetallic electrocatalysts.

C-C Coupling Selectivity

The total current efficiencies for C1, C2, and C3 products (requiring >2e⁻) are compared for the Cu(111), (751), and (100) surfaces. The enhancement in C-C coupling on Cu(751), in comparison to Cu(111), demonstrates that step sites are selective for C-C coupling.

Oxygenate Selectivity

The oxygenate/hydrocarbon ratios (requiring >2e⁻) are plotted for Cu(111), (751), and (100) vs potential to compare the oxygenate selectivities for each surface. At low overpotentials, Cu(751) has the highest oxygenate/hydrocarbon ratio, indicating that step sites are more selective for oxygenates than terrace sites.

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