Level 3 Milestone: T(1)3.1 Establish detailed understanding of mechanisms, intermediates, and reaction environments for effective CO2RR electrocatalysts.

Electrochemical Flow Reactor for Operando Attenuated Total Reflection Surface Enhanced Infrared Spectroscopy

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Abstract:

An electrochemical flow reactor for operando attenuated total reflection infrared spectroscopy (ATR-IR) has been developed and tested. Gold catalyst thin films, exhibiting surface enhanced infrared absorption (SEIRA), are prepared on ATR silicon crystals as a model system to study the electrochemical CO_2 reduction reaction (ECO_2RR). Operando spectroscopy concurrent with product collection and electrolyte flow is done during ECO_2RR at several potentials. Operando spectra shows a decrease in CO_2 concentration and increase in pH near the catalyst surface with the application of more cathodic potentials. The effect of electrolyte flow on mass transport is explored experimentally and with 1D mass transport modeling; activity and selectivity for ECO_2R are also compared to a reactor without flow.

Introduction

The selectivity and activity of electrocatalytic reactions at catalyst-electrolyte interfaces are tuned by local conditions as well as mass transport, and vice-versa. To probe this relationship, we developed an electrochemical flow reactor for operando attenuated total reflection infrared spectroscopy (ATR-IR). Understanding this relationship will enable the design of more cost-effective electrochemical reactors based on reactions like ECO_2R.

Outlook

- Further improvements in sensitivity by thin-film engineering or nanoantenna array fabrication will allow for pH measurement and reaction intermediate detection, respectively.
- Future experiments will probe the ECO_2RR with various catalysts and electrolytes, as well as other electrochemical reactions.
- Testing effects of electrolyte flow rates on product distribution coupled with 2D transport modeling and electrokinetic analysis.

Team

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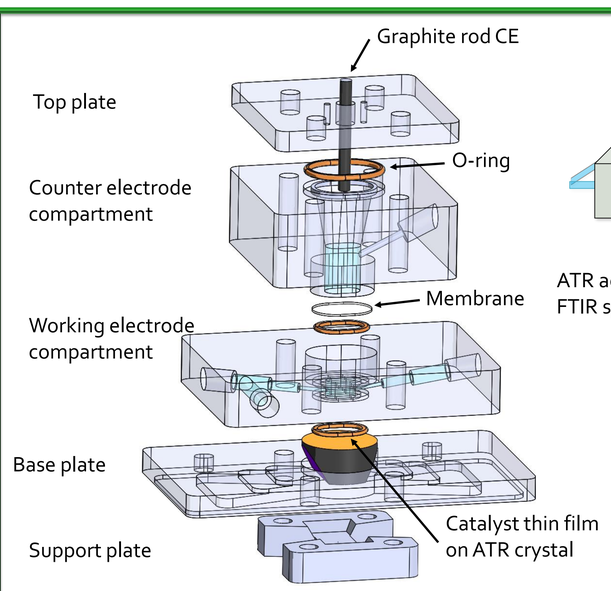
Acknowledgement

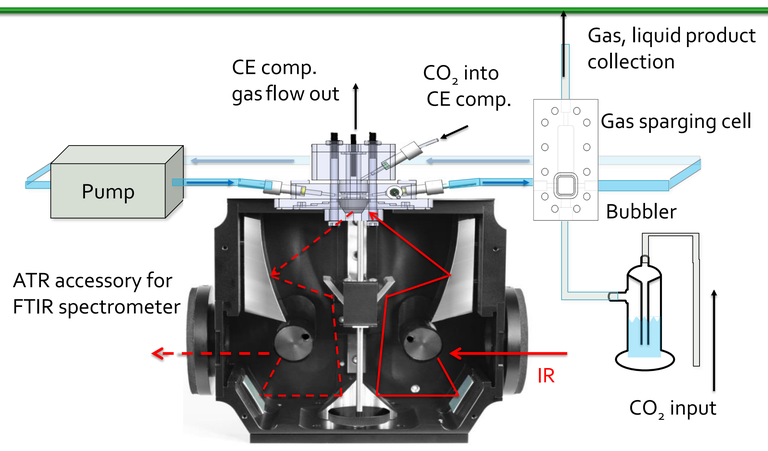
This work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of U.S. Department of Energy under Award Number DE-SC0004993. Also supported by the SUNCAT Center for Interface Science and Catalysis at SLAC and Stanford; the Stanford Nano Shared Facilities (SNSF), supported by the National Science Foundation under Award ECCS-1542152.

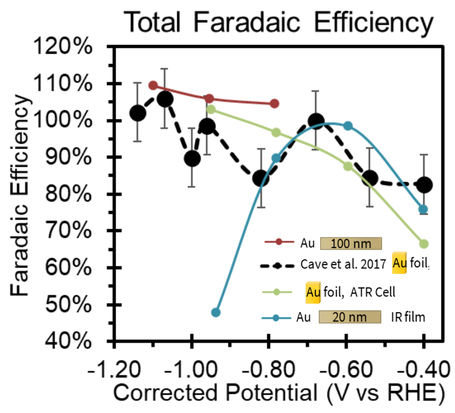
Results, Highlights, and Accomplishments

Broad impact: As greenhouse gas emissions continue to rise, the need for carbon negative technologies follows. Among many is electrochemical CO_2 reduction (ECO_2R) electrolyzers with the potential to turn this greenhouse gas into commercially useful chemicals including liquid fuels. To improve cost-efficiency, a deeper understanding of how the reaction can be controlled by catalysts and their environment is needed—advanced spectroscopy experiments are needed to reveal the relationship between these, and the reaction products collected from ECO_2R. This reactor aims to help fill that gap in knowledge with systematic studies.

Electrochemical Reactor Design





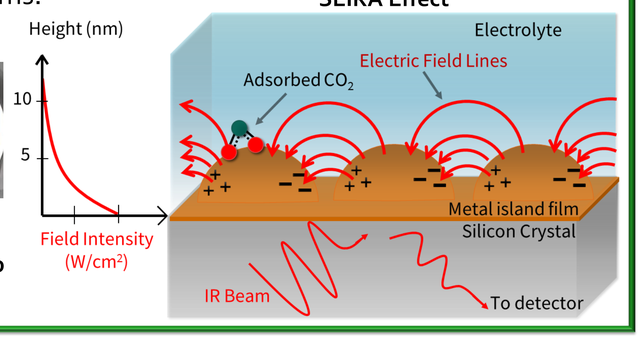


- Reactor has machinable design; choose the reactor material according to desired experimental conditions.
- Electrolyte flow for enhancing mass transport, e.g. supplying CO_2 for reaction and removing reaction products.[1] Reaction conditions can be tuned with electrolyte flowrate too.
- During shown experiments, constant potential is applied with 40 mL/min electrolyte flowrate.
- Product collection from sparge cell allows correlation of products with operando spectra.
- Top right plot shows product collection efficiency compared to a reactor without flow in black.[3]

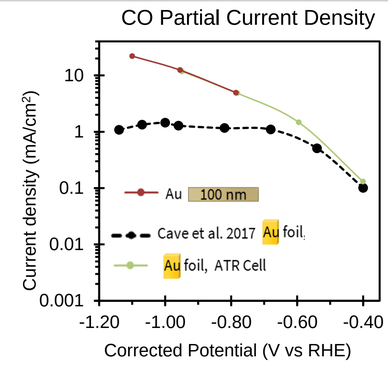
Catalyst thin film synthesis

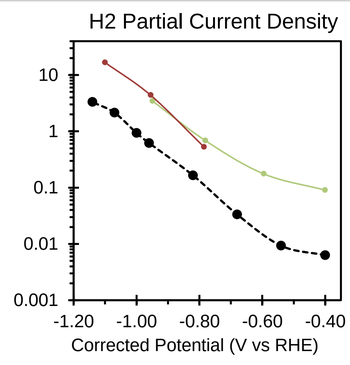
Sensitivity is achieved due to surface enhanced infrared absorption (SEIRA) effect. When sub-wavelength metal structures are closely spaced, localized surface plasmons will induce enhanced near fields that decay strongly within 10 nm of the surface but greatly increase light absorption by nearby species.[4] E-beam PVD is used to synthesize 20 nm Au thin films that exhibit the SEIRA effect.[2] These films survive higher current densities and cathodic potentials beyond -1.0V vs RHE, in contrast to chemically deposited films.

Thin film stable after >4 hours of applied potential up to -1.2V vs RHE



Electrolyte flow effects

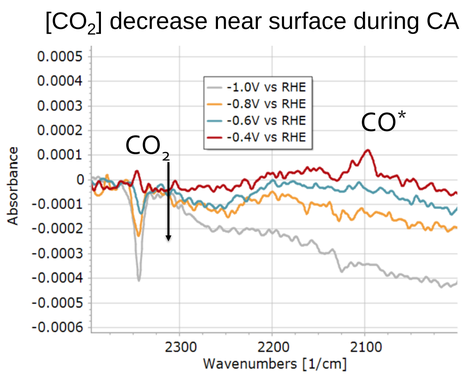


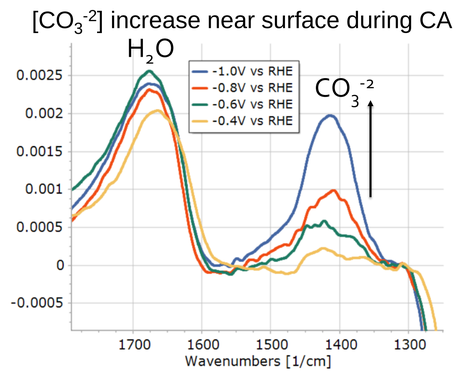


The current density towards H_2 and CO is compared between the flow reactor and a reactor without electrolyte flow.[3] The increase in current density, normalized to electrochemical surface area, is attributable to improved mass transport due to electrolyte transport.

The boundary layer thickness is calculated as a function of flowrate with the steady state current of ferricyanide reduction measured at these flowrates.[6] The pH and CO_2 concentration are calculated at the catalyst surface for the flow reactor and a reactor without electrolyte flow.[3,7]

ATR-SEIRA Spectroscopy





During chronoamperometry with the 20 nm Au thin film, we took operando spectra. Changes in the concentration of near surface species such as CO_2 and CO_3^{-2}, and changes in the interfacial water structure are seen when compared to a baseline spectra in open circuit. For this system further enhancement in sensitivity is needed to accurately quantitatively measure pH by using the HCO_3^- and CO_3^{-2} peaks' area ratio.[5]

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