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 CO₂ reduction reaction (ECO₂RR). Operando spectroscopy concurrent with product collection and electrolyte flow is done during ECO₂RR at several potentials. Operando spectra shows a decrease in CO₂ 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 ECO₂R are also compared to a reactor without flow.

**Results, Highlights, and Accomplishments**

- **Electrolyte flow effects**
  - The current density towards H₂ and CO is compared between the flow reactor and a reactor without electrolyte flow. The increase in current density, normalized to electrochemical surface area, is attributable to improved mass transport due to electrolyte flow support.
  - The boundary layer thickness is calculated as a function of flowrate with the steady state current of ferri cyanide reduction measured at these flowrates. The pH and CO₂ concentration are calculated at the catalyst surface for the flow reactor and a reactor without electrolyte flow.

**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. E-beam PVD is used to synthesize 20 nm Au thin films that exhibit the SEIRA effect. These films exhibit higher current densities and cathodic potentials beyond ~1.0 V vs RHE, in contrast to chemically deposited films.

**Electrochemical Reactor Design**

- Electrolyte flow for enhancing mass transport, e.g., supplying CO₂ for reaction and removing reaction products. 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.

**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 ECO₂RR 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.

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**References**


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