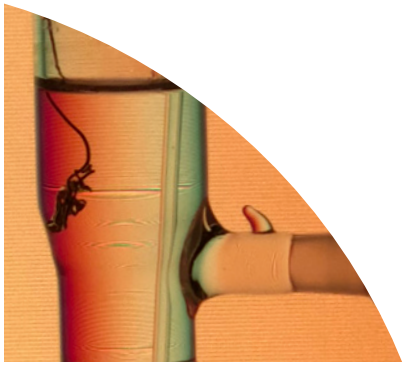
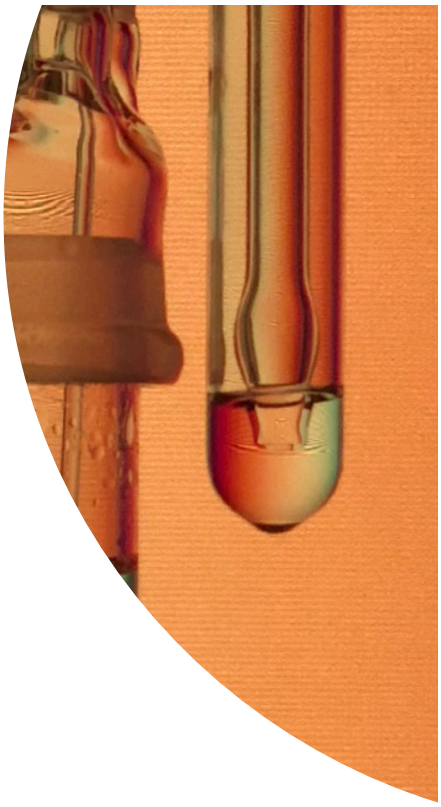
PIKE TECHNOLOGIES

Jackfish Spectroelectrochemical Cells (SEC) enable fundamental studies of the electrified metal-solution interface and applications in molecular self-assembly, interfacial sensing, and next-generation energy solutions. They are designed for surface-sensitive FTIR spectroelectrochemistry using the attenuated total reflectance surface-enhanced infrared spectroscopy (ATR-SEIRAS) technique.





JACKFISH

SPECTROELECTROCHEMISTRY CELLS

for surface-sensitive electrochemical ATR-SEIRAS

High-quality IR spectra can be obtained from sub-monolayer amounts of adsorbed molecules. By controlling the electrical potential applied to the Au thin film electrode on the ATR crystal surface, the user can perform vibrational characterization of potential-dependent changes at the interface.

Introduction to ATR-SEIRAS

Attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) is a surface-sensitive FTIR spectroelectrochemical technique which exploits the enhanced electromagnetic field produced by surface plasmon polaritons (SPPs).

How it Works

ATR-SEIRAS typically uses a Si internal reflection element coated with a thin (ca. 20 nm) layer of a noble metal such as gold. Nanoislands on the continuous metal film support surface plasmon modes which can couple to the evanescent wave generated in the ATR sampling geometry. While ATR probes roughly a quarter wavelength thick volume of bulk solution near the interface, the SPP modes generated at the metal film are highly localised to the metal-solution interface. Furthermore, the field intensity is enhanced by up to two orders of magnitude compared to the incident field, greatly increasing the absorption cross section of surface molecules. These two phenomena combine to make ATR-SEIRAS a surface-sensitive technique with submonolayer sensitivity.

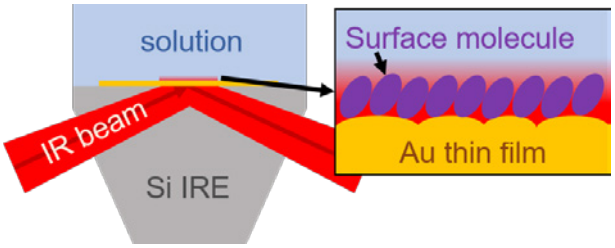
Although originally developed using Ag and Au metal films, the enhancement mechanism in ATR-SEIRAS is not limited to coinage metals. Electrochemical ATR-SEIRAS can be done on a wide range of metals.

By controlling the interfacial potential of the Au film using a standard three electrode configuration, electrochemical reactions can be studied with molecular detail. The state of the Au/solution interface can be studied at equilibrium by static potential difference measurements or in kinetic conditions by time-resolved methods following an applied potential step.

Experimental Requirements

Metal Deposition

The key to successful ATR-SEIRAS is the metal film electrode. There are two ways to deposit the film. Physical vapour deposition methods, e.g. sputtering or thermal evaporation, use high-vacuum chambers and allow control of rate and thickness to achieve the necessary nanostructure. Chemical ("electroless") deposition uses an aqueous solution of gold salt precursor, sulfite, and thiosulfite to chemically modify a hydrogen-terminated Si surface.



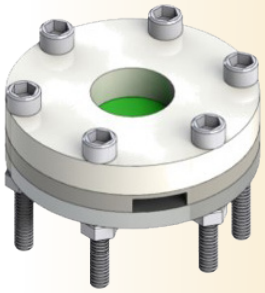
Electrochemistry

The cleanliness and nanostructure (and thus enhancement factor) of the film can be improved by an electrochemical cleaning step where the Au film is carefully cycled into oxidizing potentials over a short period. With choice of suitable electrolyte, this can promote the formation of ordered (111) domains, allowing spectroscopic investigation of primarily single crystalline surfaces.

Jackfish Spectroelectrochemical Cells are miniaturized three electrode cells which are compatible with a wide range of electrolyte solutions. The Teflon and glass design ensure that they can stand up to the rigorous cleaning procedures used by electrochemists.

Spectroscopy

The coupling between the incident infrared beam and the metal surface plasmon modes is highest near 70 degrees from the interfacial normal. This can be easily set using the PIKE VeeMAX III variable angle ATR accessory. No other special instrumentation is needed besides a research quality FTIR instrument.



Electroless Deposition Fixture

Did You Know?

You can do ATR-SEIRAS even if you don't have access to a physical deposition chamber for metal coating. SEIRAS active metal films can be made using wet chemistry techniques† and the Jackfish electroless deposition unit.

† H. Miyake, S. Ye and M. Osawa. Electrochem. Comm. 2002. 4: 973.

The Founders of Jackfish

Jackfish SEC was established in 2018 in Saskatoon, Canada by electrochemists at the University of Saskatchewan. The team has spent 10 years designing, innovating and testing spectroelectrochemical cells for attenuated total reflectance surface-enhanced infrared spectroscopy (ATR-SEIRAS). A decade of experiment-based design improvements have led to their innovative and commercially available ATR-SEIRAS cell design. They are dedicated to making advanced infrared spectroelectrochemical technology easily accessible to new users with off-the-shelf solutions that allow you to easily equip your laboratory with ATR-SEIRAS capabilities.

Electrochemical Cleaning for Improved SEIRAS Performance

After deposition of gold on a Si internal reflection element (IRE), electrochemical cleaning is required to obtain a SEIRAS active gold layer. The guidelines below give a brief description on how to perform electrochemical cleaning and determine the SEIRAS activity of a gold thin film using acetate adsorption.

Prepare and Purge Solutions

Use 50–100 mM acetate buffer as electrolyte with a pH range between 3.6 and 5.6. Choose a solution acidity similar to the experimental conditions that will be used after completing the cleaning procedure. Using an inert gas, purge the electrolyte for at least 30 minutes using a rate of ~1–2 bubbles/second.

Cyclic Voltammetry for Electrochemical Cleaning of Gold Electrode

Measure the open circuit potential (OCP).

Cyclic voltammetry (CV) parameters:

Starting potential: OCP
Potential window: ±200 mV from the OCP
Scan rate: 20 mV/sec

Complete three cycles at this potential window, increase the positive limit by 100 mV and perform an additional three cycles. When the positive limit has reached +600 mV (vs Ag/AgCl) start monitoring the IR activity of adsorbed acetate following the steps outlined below.

IMPORTANT: Ensure not to enter hydrogen evolution as this will be detrimental to the gold film.

IR Monitoring of Acetate Adsorption during Cleaning

The symmetric COO^- stretching of acetate adsorbed on gold is observed at 1400 cm^{-1}. The potential dependence of acetate adsorption/desorption on the gold surface is an indication of the SEIRAS activity of the gold layer. Use the following method during the electrochemical cleaning procedure.[1]

Start monitoring acetate adsorption/desorption as the positive potential limit extends beyond +600 mV (vs Ag/AgCl). After three cycles at each potential window hold the potential at -100 mV (vs Ag/AgCl) for reference potential and +600 mV (vs Ag/AgCl) for sample potential. Measure an IR spectrum at each of the sample and reference potentials. Monitor COO^- stretching vibration at 1400 cm^{-1} and continue the electrochemical cleaning.

This is a delicate balance to determine the appropriate amount of electrochemical cleaning. Monitor the COO^- stretching vibration with each potential window increase and continue the cleaning procedure until the COO^- band reaches a maximum. If the acetate signal remains steady and SEIRAS signal is undesirably low, two methods of cleaning can be used: prolonged cycles in the current potential window or extending the window further into gold oxidation. Closely monitor the potential-dependant acetate adsorption every 3–5 cycles with both methods. A decrease in acetate absorbance is an indication of film failure. Additional cycling typically will not improve the signal after a decrease.

When gold oxidation and reduction is reached in the CV, increase the potential limits by 50 mV increments. Gold oxidation typically starts at about +1.0 V (vs Ag/AgCl). Refer to Figure 1 for a typical CV of electrochemical cleaning of gold on Si IRE and the potential dependence of COO^- stretching at 1400 cm^{-1} on a clean gold surface.

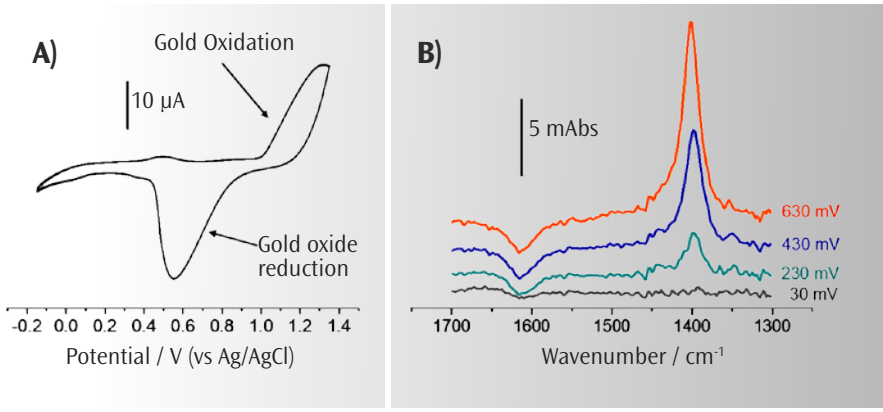


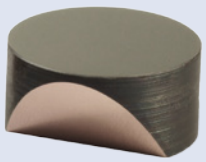
Figure 1. (a) Typical CV of gold electrochemical cleaning using acetate buffer,100 mM acetate at pH 3.6 and 20 mV/sec scan rate and Ag/AgCl reference electrode. (b) Potential dependence of symmetric COO^- stretching of adsorbed acetate on clean gold surface after electrochemical cleaning procedure. Absorbance spectrum for 630 mV, 430 mV, 230 mV, and 30 mV (vs Ag/AgCl) all referenced to -100 mV (vs Ag/AgCl).

Reference

[1]Delgado, J. M.; Orts, J. M.; Pérez, J. M.; Rodes, A. Journal of Electroanalytical Chemistry 2008, 617, 130.

Choose from Two Configurations — Face Angle or Wafer

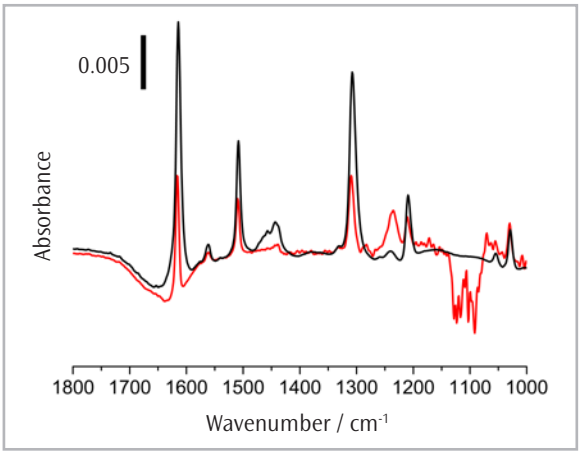
The Jackfish SEC is available in two formats to accommodate different ATR element geometries. The **Jackfish J1** is designed around the face angle prism, and the newly available **J1W** around a new low-cost Si ATR wafer. While strongly absorbing phonon modes saturate the fingerprint region of the face angle prism, the anti-reflective coating improves throughput above the low wavelength cutoff for superior signal-to-noise. The shorter pathlength through the microgrooved Si wafer allows access to the full mid-IR spectral range from 5000 to 400 cm^{-1}. Read more about the low-cost Si wafer elements in the first of the selected references below.



60 degree Si face angle prism (above). Si ATR wafer (right).

Jackfish J1 and VeeMAX III Assembly

By design, the J1 cell is fully compatible with the PIKE VeeMAX III variable angle ATR sampling accessory and face-angled crystal (FAC). In a previous study investigating the adsorption of a pyridine derivative, the spectral response was two times stronger when using a Si 60 degree FAC compared to a Si hemisphere with an angle of incidence of 65 degrees. Additionally, the FAC exhibited higher energy throughput and lower spectral noise.



Comparison of electrochemical ATR-SEIRAS response with the VeeMAX III Si 60 degree FAC (black) and a Si hemisphere (red). Sample spectrum is of the Au thin film electrode covered in a monolayer of adsorbed pyridine derivative at positive potential; reference spectrum is taken at negative potential where the pyridine is completely desorbed.

Selected References from the Jackfish Team

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Surface Enhanced Infrared Absorption Spectroscopy Studies of DMAP Adsorption on Gold Surfaces. Langmuir, 2009, 25, 2241-2247.

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PIKE TECHNOLOGIES

Ph: (608) 274-2721
E-mail: info@piketech.com
Web: www.piketech.com

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