Monitoring Electrochemical Performance of SEIRAS Gold Layers

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

Figure 1. The Jackfish SEC assembled on the VeeMAX III variable angle, single reflection ATR from PIKE Technologies.

After deposition of gold on a Si IRE electrochemical polishing is required to obtain a SEIRAS active gold layer. Measuring the adsorption of acetate on the gold surface is a good determination of this activity. The guidelines below give a brief description on how to perform electrochemical polishing and determine the IR activity of a gold thin film using acetate adsorption.

Prepare Solutions

Use 50–100 mM acetate buffer as electrolyte with a pH range between 3.6–5.6. Choose a pH similar to the experimental conditions that will be used after completing the polishing procedure.

Purge Electrolyte

Fill the cell with the acetate electrolyte. Use an inert gas purge for removal of dissolved oxygen. Purge the electrolyte for at least 30 minutes using a rate of ~1–2 bubbles/second.

Cyclic Voltammetry for Electropolishing of Gold Electrode

Measure the open circuit potential (OCP). For a gold coated IRE and a Ag/AgCl (saturated KCl) reference electrode the solution OCP is typically ~100 mV.

CV parameters:

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

Complete three cycles at this potential window, then increase the positive limit by 100 mV and perform an additional three cycles at the new potential limits. When the positive limit has reached +600 mV (vs Ag/AgCl) start monitoring the IR activity of adsorbed acetate following the guideline 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}. Monitor the potential dependence of acetate adsorption/desorption on the gold surface as an indication of the SEIRAS activity of the gold layer using

the following method during the electrochemical polishing procedure.[1]

Start monitoring acetate adsorption/desorption as the positive potential limit extends beyond +600 mV (vs Ag/AgCl). After 3 cycles at each potential window hold the potential at:

- -100 mV (vs Ag/AgCl) – reference potential
- +600 mV (vs Ag/AgCl) – sample potential

Measure an IR spectrum at each of the above potentials and determine the absorbance of acetate adsorption. Monitor COO^- stretching vibration at 1400 cm^{-1} and continue the electrochemical polishing until this band reaches a maximum. This is a delicate balance to determine the appropriate amount of electropolishing. By monitoring the COO^- stretching vibration with each potential window increase, determine if the absorbance is continually increasing. A decrease in the acetate absorbance is an indication of film failure. Additional electropolishing typically will not improve the signal after a decrease. If the acetate band remains steady two options are available; prolonged cycling or extending the potential window. With either option ensure to closely monitor the potential dependant acetate adsorption every 3–5 cycles. As a first option, try prolonged cycling to improve signal. If no improvement is made extend the potential window further into gold oxidation.

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 2 for a typical CV of electrochemical polishing of gold on Si IRE and the potential dependence of COO^- stretching at 1400 cm^{-1} on a clean gold surface.

Reference

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

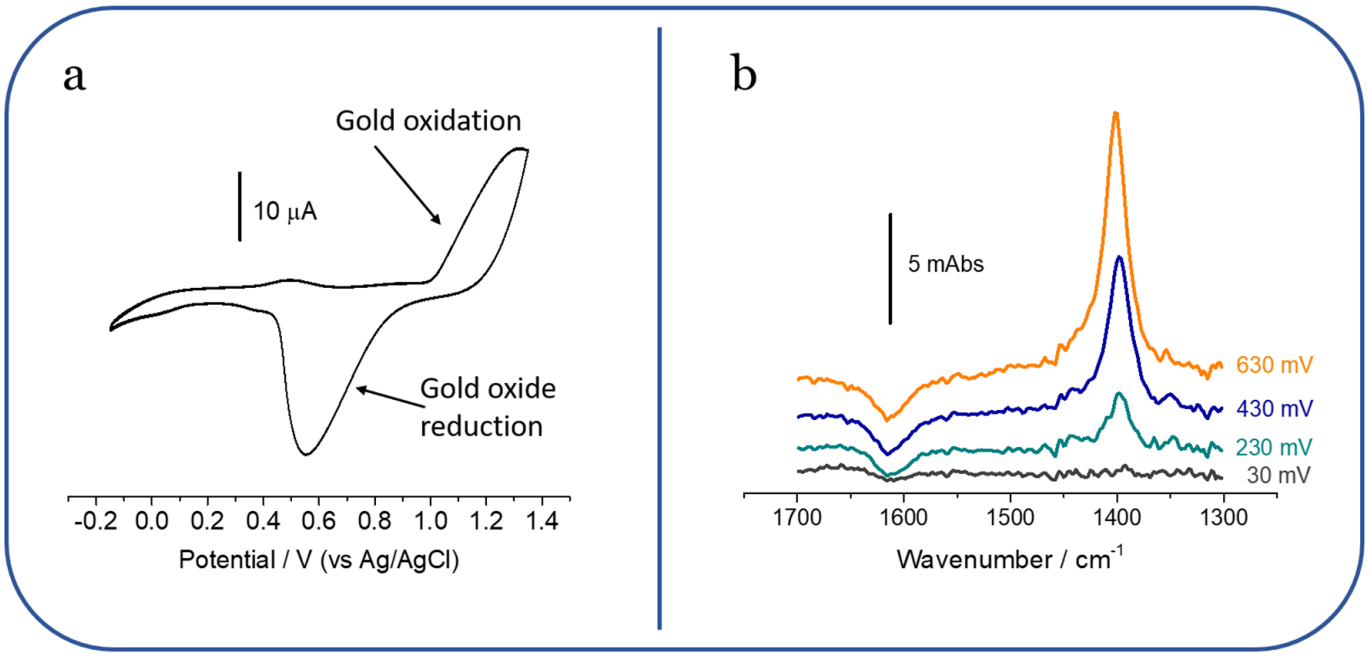

Figure 2. (a) A typical CV of gold electropolishing using acetate buffer, using 100 mM acetate at pH 3.6 and a 20 mV/sec scan rate and Ag/AgCl reference electrode. (b) Potential dependence of symmetric COO^- stretching of adsorbed acetate on clean gold surface after electropolishing procedure. Absorbance spectrum for 630 mV, 430 mV, 230 mV, and 30 mV (vs Ag/AgCl) are all referenced to -100 mV (vs Ag/AgCl).