Electrochemical Methods for the Determination of Redox Properties for Self-Assembled Monolayers of Thiol-Terminated Porphyrin

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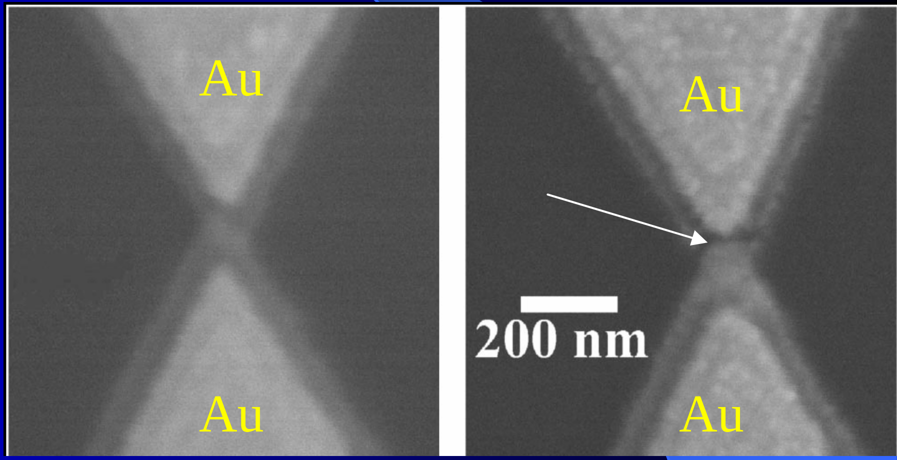
Introduction

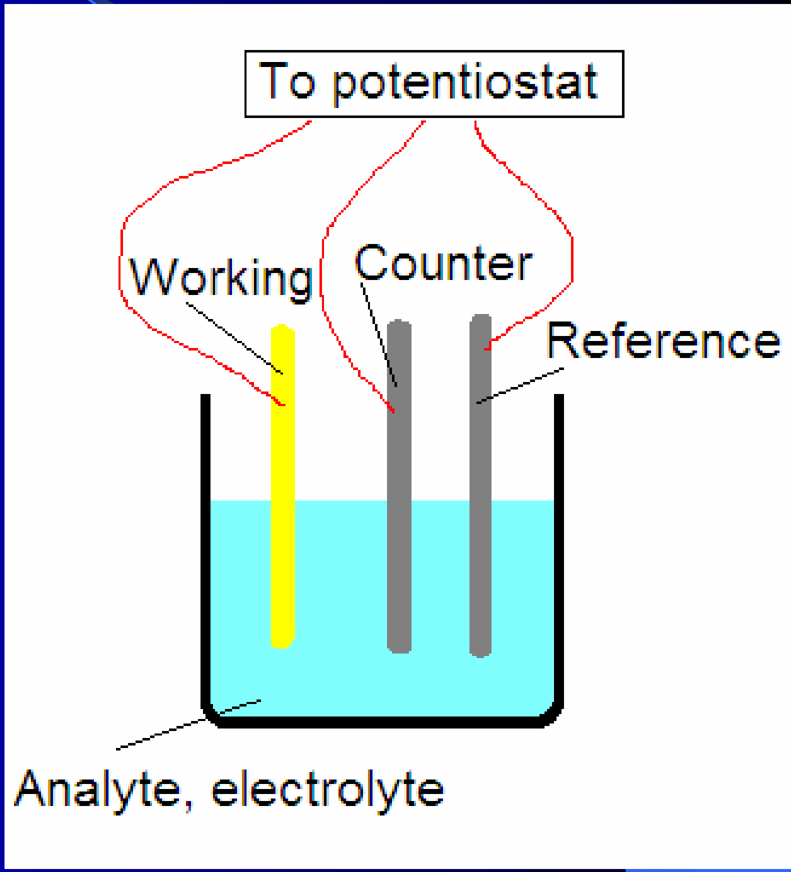
- Molecular electronics: the use of single molecules as conducting channels in electronic devices.
- Small size scale, promise for high speed
- Advances being made: nanogaps between two gold leads, wide enough to fit a molecule
- How does a molecule react chemically when bonded to gold?

Before After

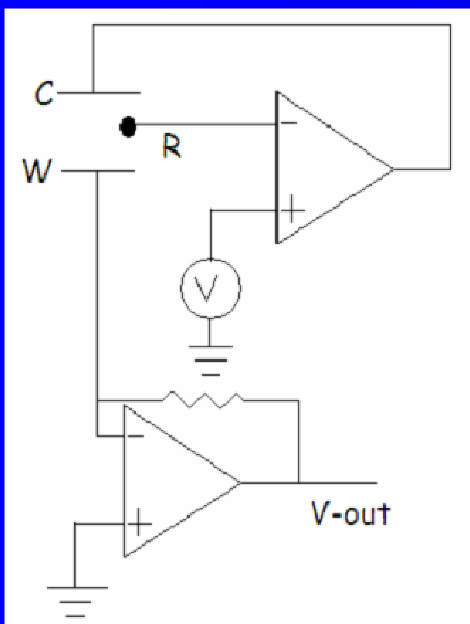


Three-Probe Electrochemistry Setup

- Changing voltages yields certain reactions in the analyte
- Want to measure the current produced by these reactions
- Working electrode (gold): business end
- Counter electrode (silver): injects current
- Voltage is regulated between working and reference electrodes



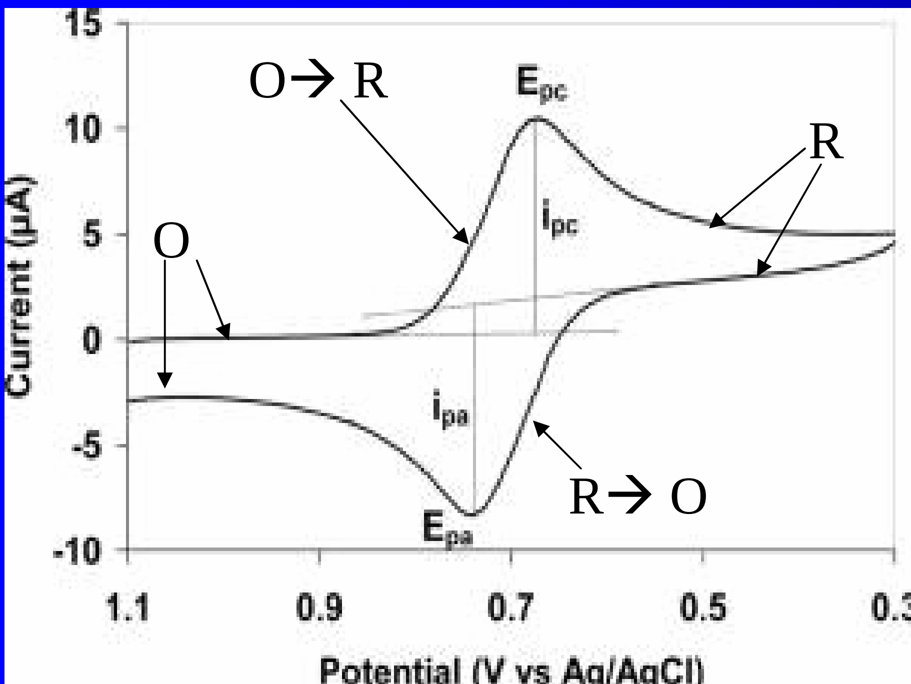
The Potentiostat*



- Potential drop between reference and working electrodes kept at V_{ref}.
- Counter electrode outputs current necessary to maintain V_{ref}.
- Current-to-voltage converter outputs V_{out} to computer.
- Inexpensive, versatile
- We can set our own parameters with our own potentiostat

*Thanks to Sujit Datta (Johnson group, Penn) for technical assistance with the construction of the potentiostat.

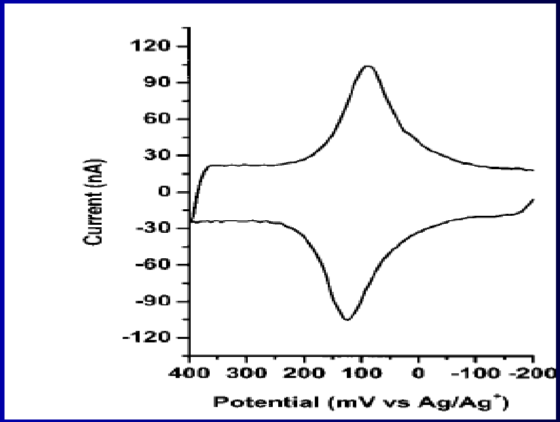
Cyclic Voltammetry



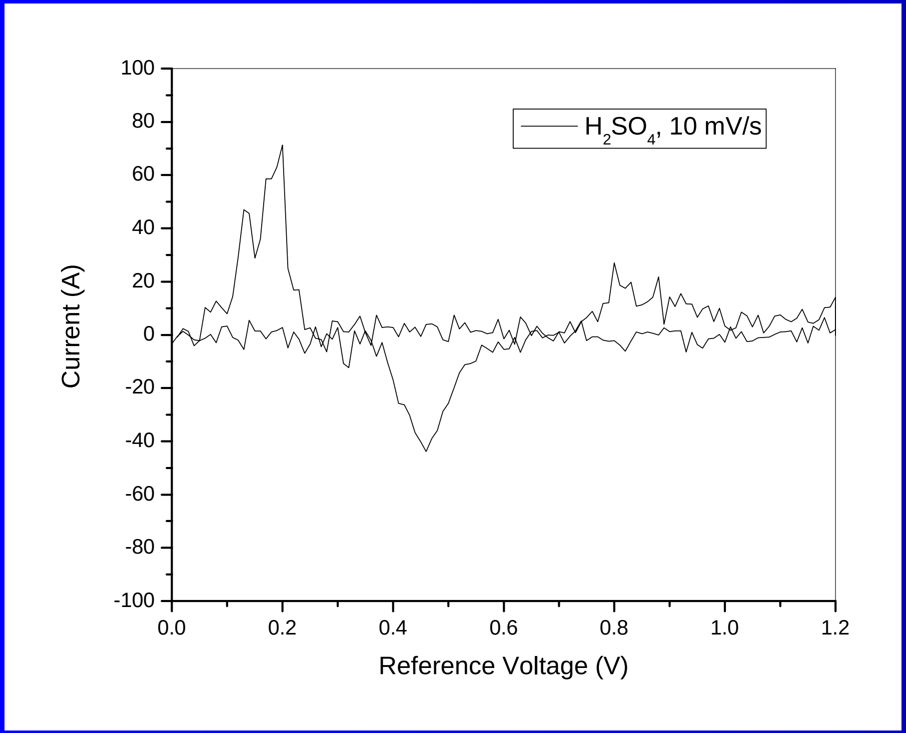
- Mechanism: $O + e^- \rightarrow R$
- Raising the voltage causes the reaction to occur, which creates a current.
- Diffusion limitations for reversible
- Peak separation indicates whether or not reaction is reversible
- For SAM, no diffusion limitations

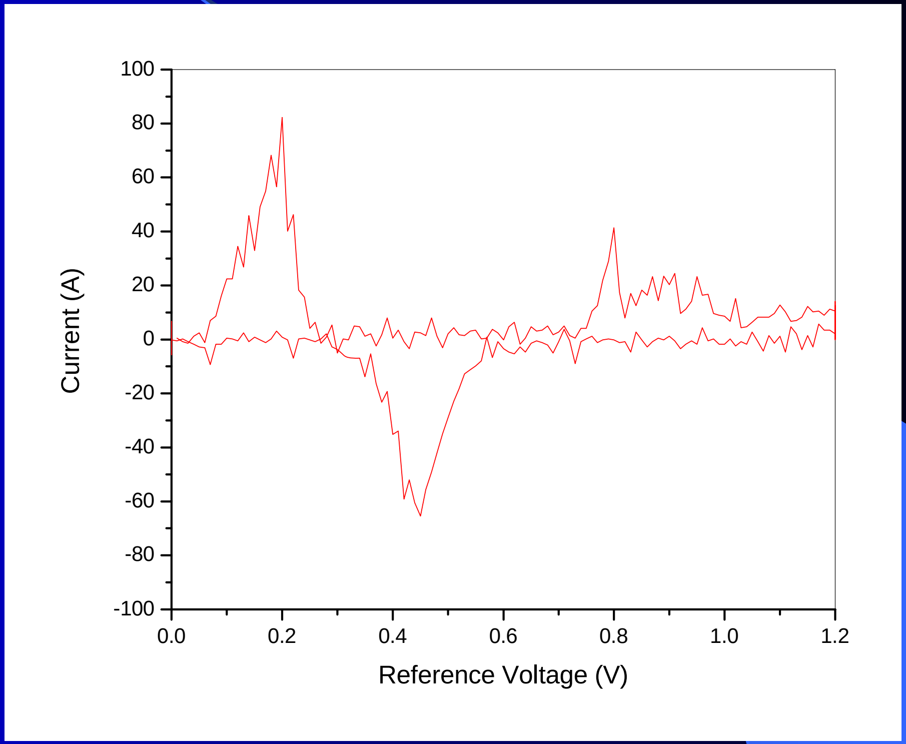
Above: Idealized reversible reaction

Right: Idealized SAM



0.1 M Sulfuric Acid, 10 mV/s

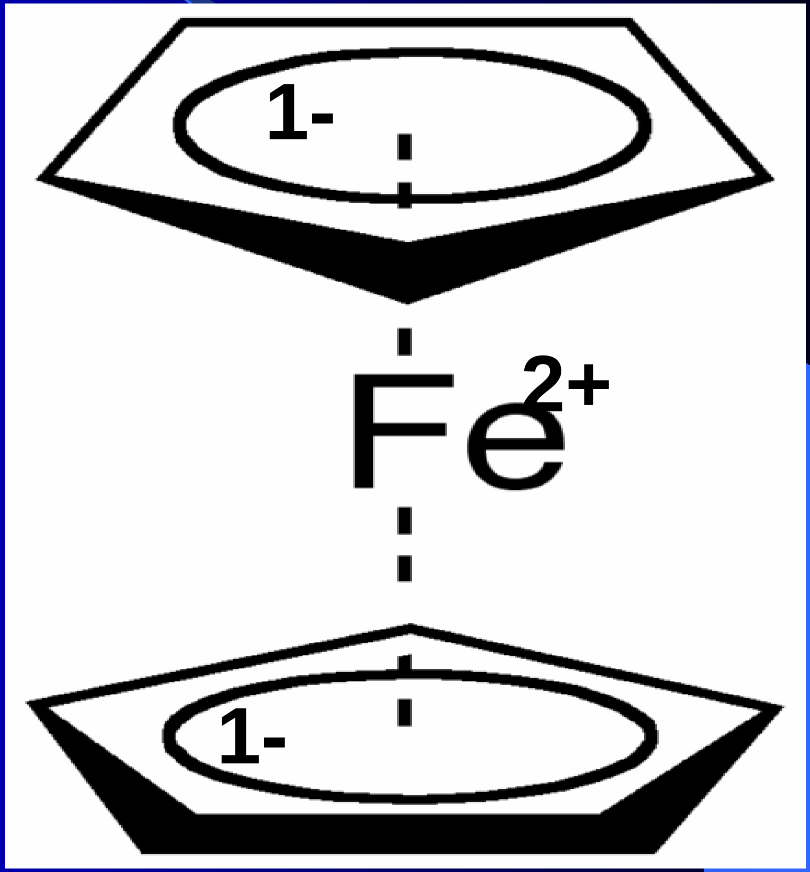




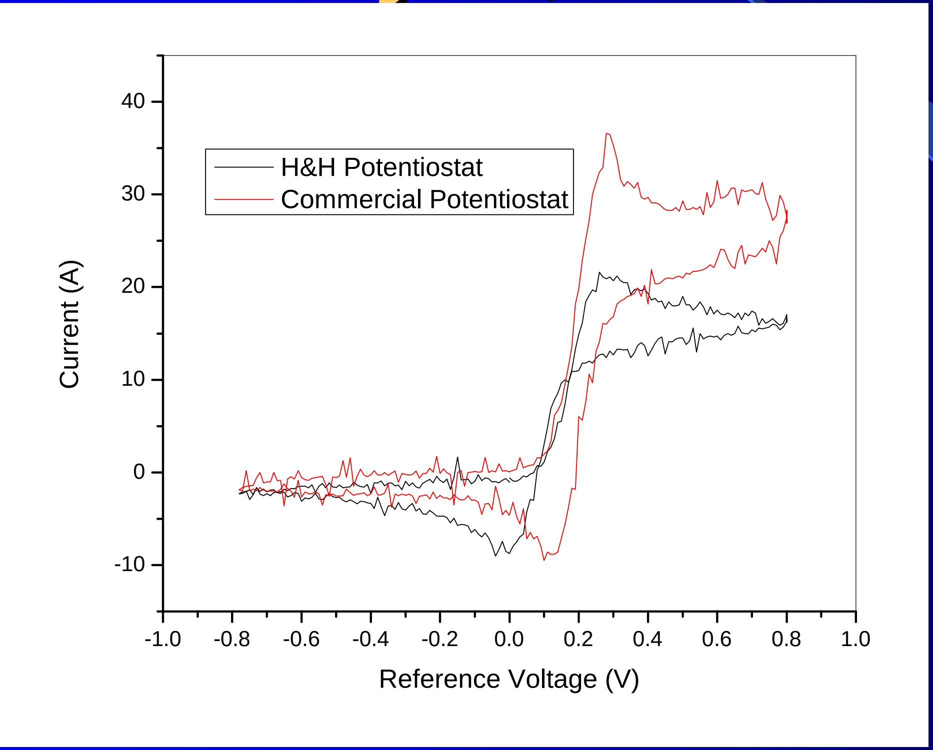
- Red: cyclic voltammogram using PAR potentiostat
- Black: cyclic voltammogram using H&H potentiostat

Ferrocene

- Very well known compound, good for background testing
- Reaction: $Fe^{2+} + e^{-} \rightarrow Fe^{3+}$
- Reversible reaction, expect peak separation to be close and constant

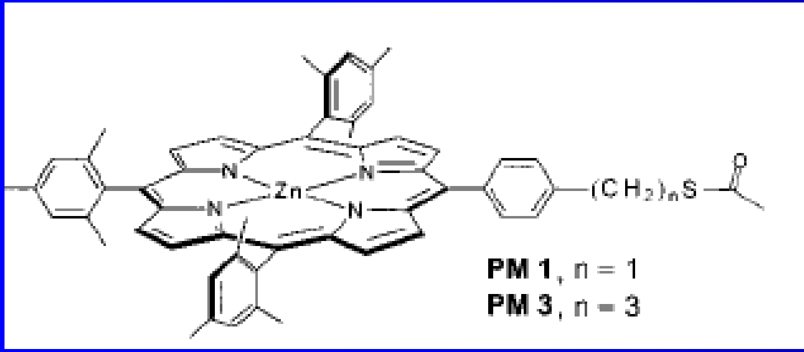


Ferrocene in 0.1 M organic electrolyte, 10 mv/S



- Black: PAR, Red: H&H
- Peaks of both plots show that the ferrocene compound is reversible (~200 mV peak separation)

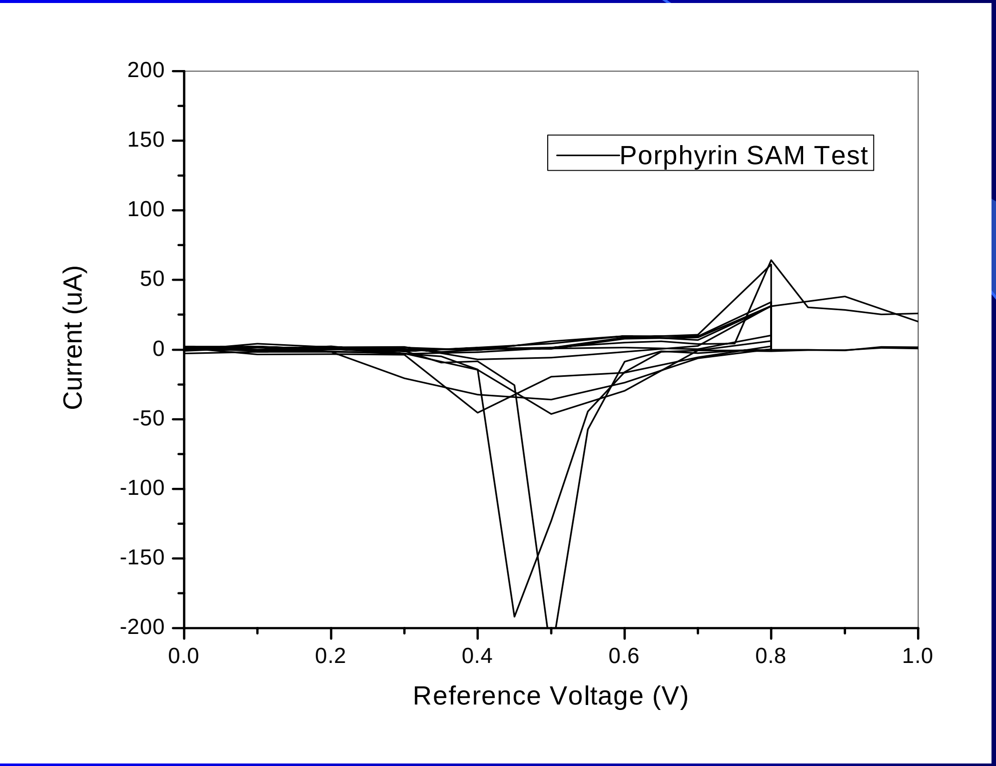
Porphyrin



- Strong, bonds to gold layer well
- Most commonly used bond for SAMs.

- Creates self-assembled monolayer (SAM) on Au electrode.
- Thiol bond strength: ~160 kJ/mol
- Covalent bond strength: ~400 kJ/mol
- Hydrogen bond strength: ~20 kJ/mol

Porphyrin SAM Test



- A self-assembled monolayer could not be detected from this cyclic voltammogram data.

Future Steps

- For the detection of SAMs
  - Faster scan rate
  - Larger gold electrode surface area
- After SAM detection
  - Insert molecules into nanogap
  - Adapt methods to determine electrochemical properties in porphyrin bonded to gold on both ends.

Conclusions

- Constructed inexpensive, versatile potentiostat for regulating voltage
- Tested against commercial potentiostat
- Made electrochemical setup to determine redox reactions in sulfuric acid and ferrocene
- Ran a test for the detection of porphyrin SAMs.

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