Control of Electrochemical Activity with Thermally Responsive Polymers

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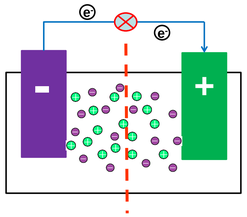
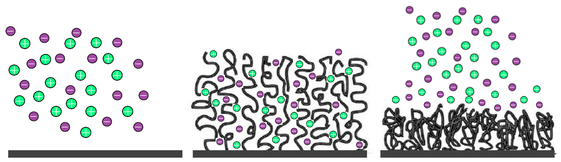
Introduction

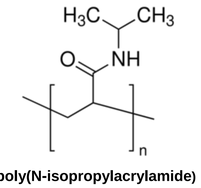
- Electrochemical systems such as batteries rely on ion transport at an electrode surface.
- Smart systems with variable electrochemistry dependent on temperature could be used in batteries and biosensors.
- Thermally responsive polymers change structure at a lower critical solubility temperature (LCST).



Objectives

- Goal: To modify and electrode surface with poly(N-isopropylacrylamide), PNIPAM, to create a thermally responsive surface.
- Hypothesis: A PNIPAM layer will limit electrochemistry at elevated temperatures while scarcely affecting it at lower ones.

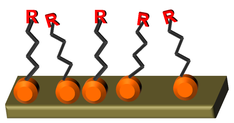




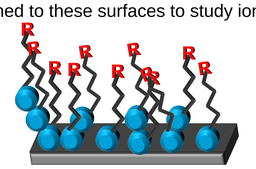
poly(N-isopropylacrylamide)

Experimental Methods

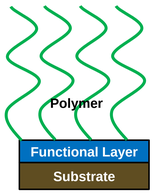
Gold and ITO surfaces were modified with thiol and silane chemistries to produce a grafting layer with an amine functional end group. Carboxyl terminated PNIPAM and a copolymer of PNIPAM and acrylic acid were separately attached to these surfaces to study ion transport effects.



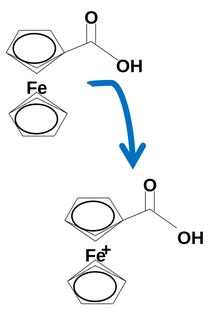
Aminoethanethiol Hydrochloride on Gold



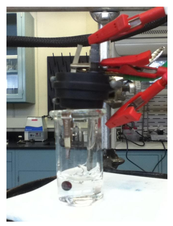
Aminopropyltriethoxysilane on ITO



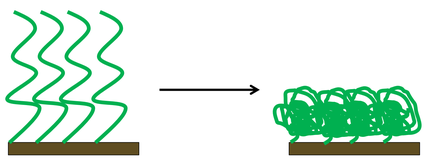
The surfaces were characterized with cyclic voltammetry (CV) using ferrocene carboxylic acid above and below LCST using a three-electrode configuration. CV was used to measure changes in ion transport at the surface by measuring redox activity.



Ferrocene Oxidation



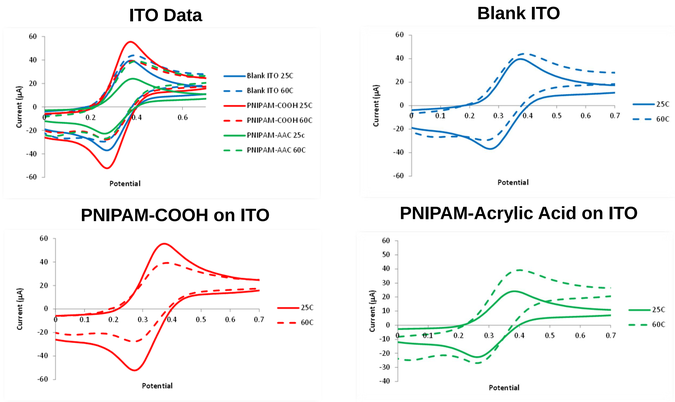
Three-electrode Configuration



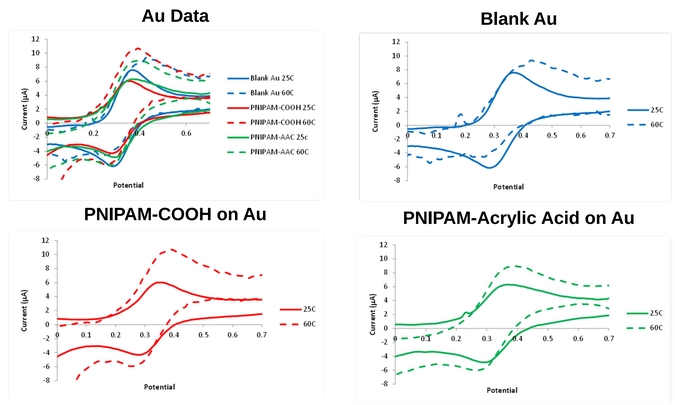
LCST Transition

Polyaniline (PANI) electrodes were polymerized at constant potential. Polyglycidyl methacrylate (PGMA) was synthesized radically. The PANI electrodes were dip coated in PGMA and annealed. A PGMA coated electrode was then dip coated in carboxyl terminated PNIPAM and another in the PNIPAM copolymer, then annealed. Both were characterized using sulfuric acid above and below the LCST.

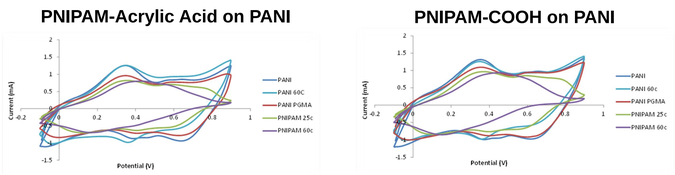
Results



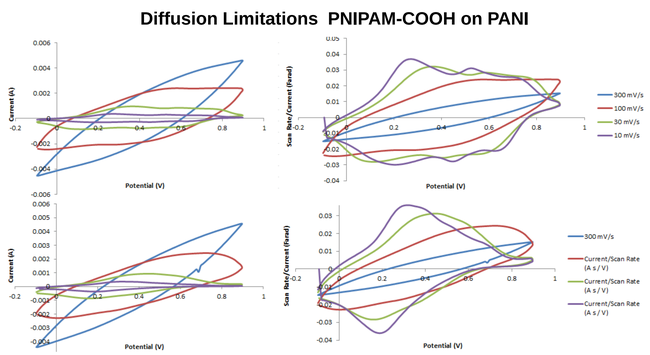
CV of ITO in Ferrocene CA at 30mV/s against a Ag/AgCl Reference



CV of Au in Ferrocene CA at 30mV/s against a Ag/AgCl Reference



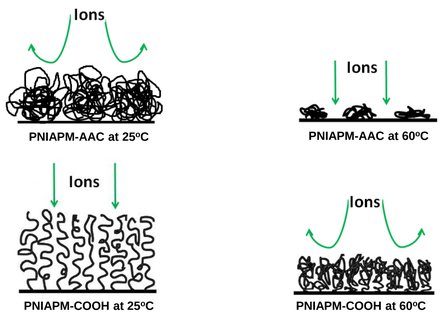
CV of PANI in sulfuric acid at 30mV/s against a Ag/AgCl Reference



CV of PANI in sulfuric acid at multiple scan rates

Discussion

- Data shows a minor change in electrochemistry with respect to temperature in the blank ITO as well as blank Au.
- Oxidation peaks are more pronounced on ITO with COOH terminated PNIPAM at room temperature, but worsen with LCST transition.
- Oxidation peaks are more pronounced on ITO with PIPAM/acrylic acid copolymer after LCST transition, but are less defined at room temperature.
- All gold data shows an increase in redox activity with increase in temperature, but gold substrates are older and yield less reliable data.
- Copolymer geometry possibly creates larger radius of gyration inhibiting ion diffusion at low temperatures but shrinks to allow diffusion at high temperatures.
- PNIPAM chains with functional end possibly form a brush that becomes more dense after transition inhibiting ion diffusion.
- PANI shows electrochemical loss after LCST for both polymers, but more pronounced for COOH terminated. As the overall change is greater and the same for both polymers it is expected surface density of the polymer affects changes in ion transport.



Conclusions.

- Electrode surfaces can be modified and the electrochemistry altered using thermally responsive polymers.
- Electrodes can not only be modified to inhibit electrochemistry at elevated temperatures as hypothesized, but also at lower temperatures allowing for either thermally controlled system: on at cold and off at hot, or off at cold and on at hot.
- Surfaces were not fully controlled, only slightly altered. Further research must be done to develop into practical application.
- Different geometries and densities vary how ion transport is changed before and after LCST transition.

Future Work

- Larger molecular weight polymers can be grafted to the surface to introduce a greater surface coverage at high temperatures to increase inhibition.
- Polymers can be grafted from the surface as opposed to being grafted to in order to create a denser layer to increase inhibition.
- The surface modifier can be changed in order to create a more perfect monolayer for the polymer to be coupled to creating greater order and eliminating “holes.”

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