Ion Know Which Nafion is Better

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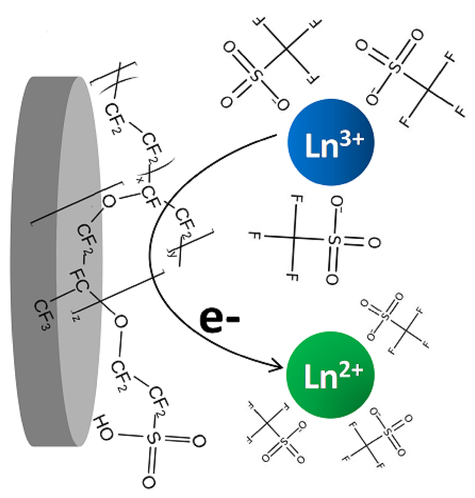
Introduction

- Part of the current theory to explain why using a Nafion film-modified platinum electrode allows for the observation of the redox behavior of lanthanide trifluoromethanesulfonate (triflate) is that Nafion solubilizes the lanthanide compounds, possibly by replacement or equilibrium of ligands with a sulfonate group.
- Nafion is a cation-exchange polymer with perfluorovinyl ether groups terminated with sulfonate groups onto a tetrafluoroethylene backbone. Triflate is a ligand that closely resembles Nafion perfluorosulfonate side chains.
- Equivalent weight (EW) is defined as the number of grams of dry Nafion per mole of sulfonic acid groups when it is in the acid form.
- Our group predicts if the lanthanide triflate interacts with the ion exchange sites on the Nafion film membrane, the membrane with more sites will have a higher current density.
- This investigation will contribute to the development of lanthanide-based catalysts and the knowledge of Nafion as ion exchange membranes.

Objectives

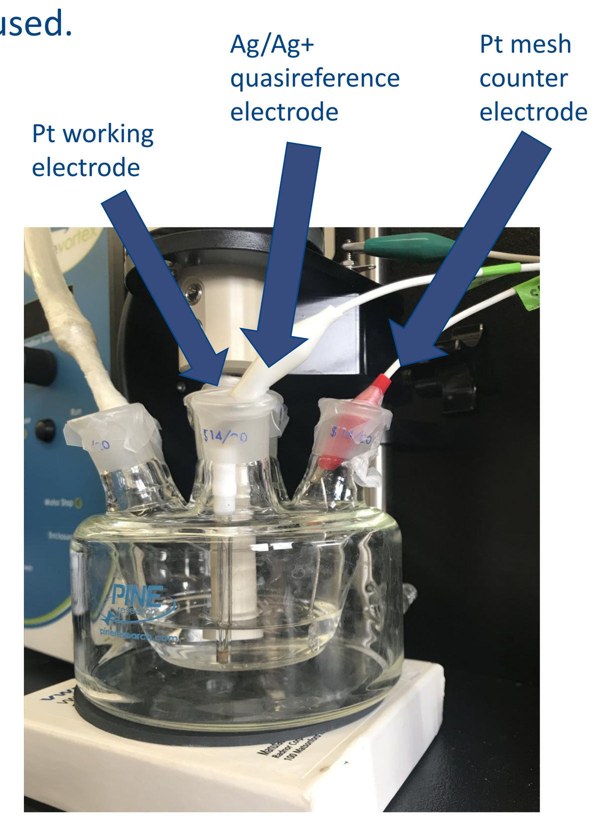
- Investigate the role of ion exchange sites in two different Nafion films by analyzing the current density of the first reduction peak in Ytterbium triflate acetonitrile solution.
- Determine how the thickness of the Nafion film applied on the working electrode affects the current density



Methods

Three Electrode System

A solution of 1 mM lanthanide (Ytterbium(III) triflate) and 0.1 M tetrabutylammonium tetrafluoroborate was poured into a three-neck cell and sealed with Parafilm. The Nafion film-modified 0.19635 cm^2 platinum working electrode, a platinum mesh counter electrode, and a silver/silver nitrate quasi-reference electrode were used.



Three Electrode Cell Setup

Cyclic Voltammetry

A potentiostat is used to generate voltammograms which measures the current and can then be analyzed to determine electron movement in the reactions.

Modified Working Electrode

The platinum electrode was polished with 1.0, 0.3, and 0.05 micron polishing powder successively. 2 or 6 μL of Nafion® 117 or Nafion® perfluorinated resin was pipetted onto the surface of the 0.19635 cm^2 platinum electrode and left to air dry for at least 24 hours leaving a polymer film.

Ferrocene

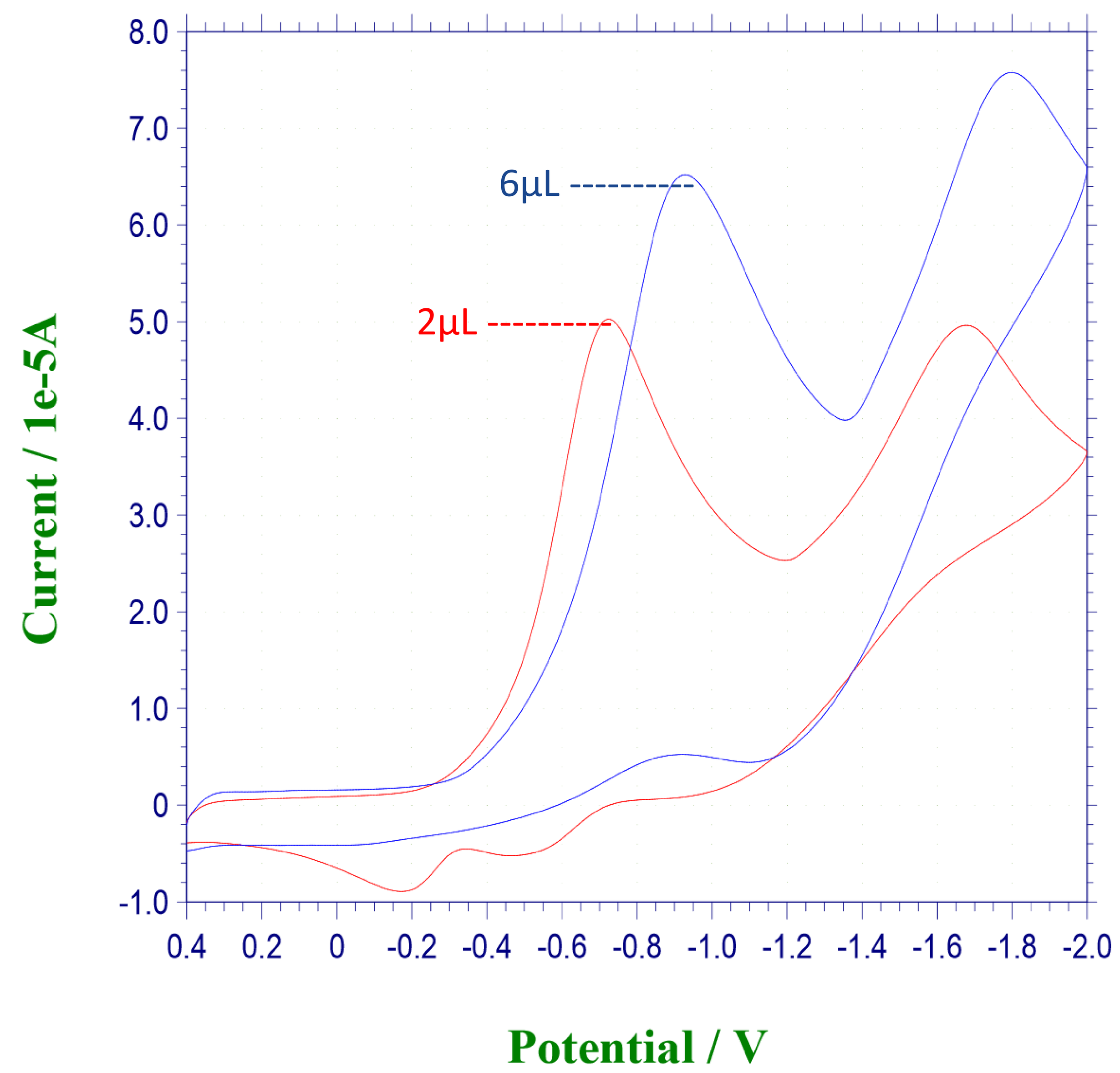
Used at the end of each experiment as an internal reference to check if the quasi-reference electrode's potential is shifting.

Nitrogen Gas

Nitrogen gas was bubbled through the solution followed by a blanket of N_2 gas prior to the first scan. N_2 gas was then bubbled in between scans to purge oxygen out of the system.

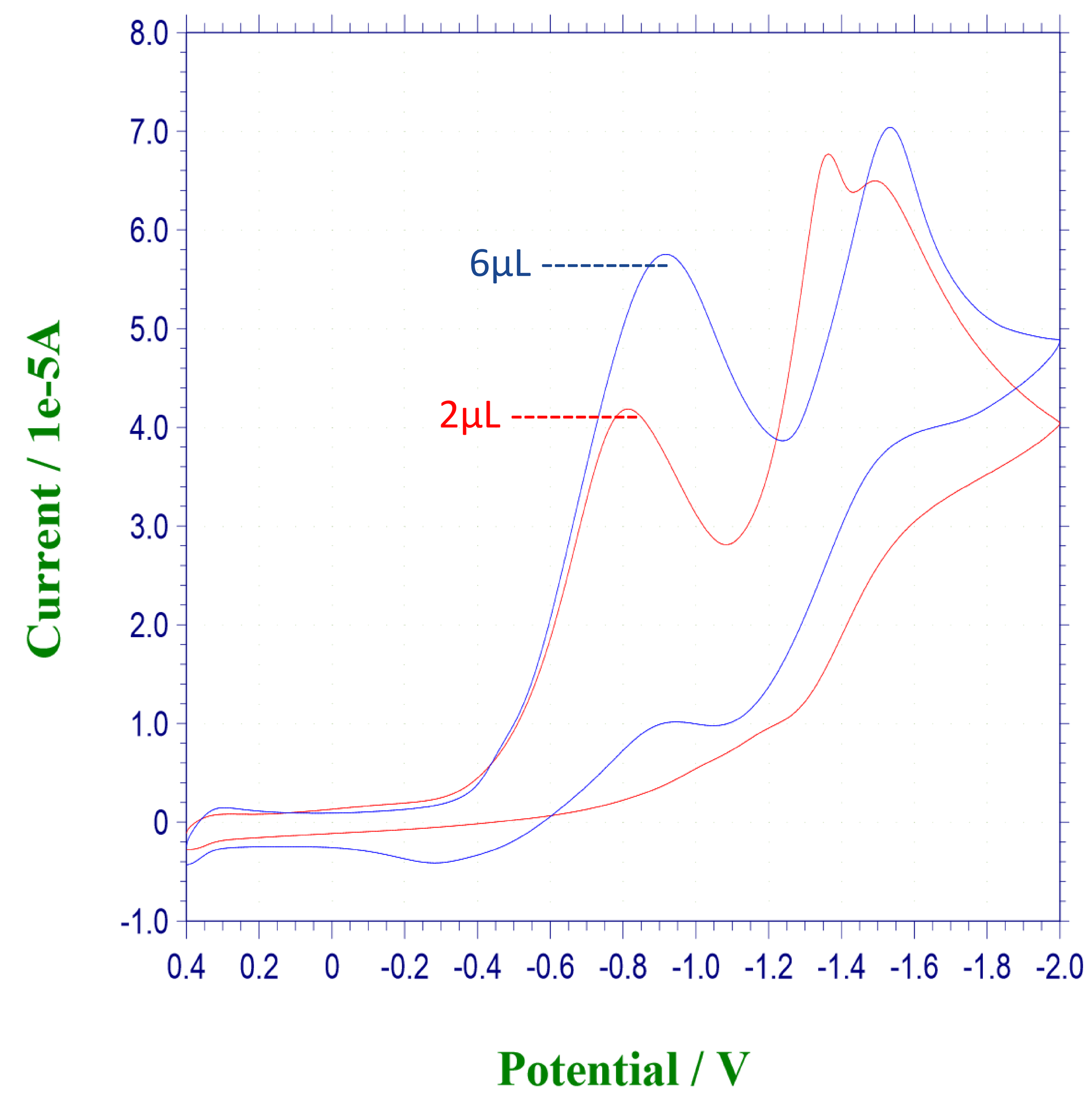
Data and Results

Nafion 117



Current density of the first reduction peak for Nafion 117 modified working electrode shows a positive correlation between current density and thickness (μL) of Nafion applied. 2μL *I*=5.031E-5 V 6μL I=6.498E-5 V

Nafion Perfluorinated Resin



Current density of the first reduction peak(for Nafion Perfluorinated Resin modified working electrode shows a positive correlation between current density and thickness (μL) of Nafion applied. 2μL *I*=4.152E-5 V 6μL *I*=5.746E-5 V

A scan rate of 50 mV/s was used throughout for both Nafion 117 and Nafion perfluorinated resin. Both types of Nafion have the same equivalent weight of 1100; however, Nafion 117 shows higher current density in the first reduction peak compared to Nafion perfluorinated resin. Nafion 117 and Nafion perfluorinated resin both show an increase in current density with an increasing amount of Nafion applied to the working electrode surface.

This is an agreement with our prediction because an increase in the amount of Nafion applied implies the polymer film will have more sites for the lanthanide triflates to interact with. It is currently unclear why Nafion 117 shows a higher current density compared to Nafion perfluorinated resin considering both have the same equivalent weight.

Type of Nafion	Amt. of Nafion (μL)	Current (1E-5 A)	Potential (V)
Nafion perfluorinated resin	2	4.152	-0.8106
Nafion perfluorinated resin	6	5.746	-0.9229
Nafion 117	2	5.031	-0.7322
Nafion 117	6	6.498	-0.9229

Table 1. Currents and potentials of the first reduction peak in the Ytterbium(III) triflate tetrabutylammonium tetrafluoroborate electrolyte system with the two types of Nafion-modified platinum working electrode. Two diffeerent amounts of Nafion were used to further analyze the influence of the thickness in polymer films on the current density.

Future Plans

- Quantitatively analyze data already gathered.
  - Calculate diffusion coefficients
  - Calculate current peak ratios
- Continue investigating the difference in the two Nafion types on the mechanism
- Collect additional data using Nafion of different equivalent weights.
- Collect additional data using polymer films of different thickness.
- Analyze more of the reduction peaks from our existing data and add to the current presented data.

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