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Nanomechanical Characterization of Fuel Cell Ionomers

Author: Jackson Goddard^{1,2} Advisor: Shudipto Dishari¹

¹Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln

²Department of Mathematics, University of Nebraska-Lincoln



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Background

Renewable Energy

- Energy sustainability can be achieved by improving and adopting clean energy technologies
- Proton exchange membrane fuel cell (PEMFC) is a promising energy conversion device.
- Better nanoscale understanding of ionomer-catalyst layers could lead to increased efficiency of PEMFCs¹
- Ion transport is related to mechanical properties, and humidity modulates the mechanical properties.** It is thus important to explore the viscoelastic properties of thin ionomer films as a function hydration level

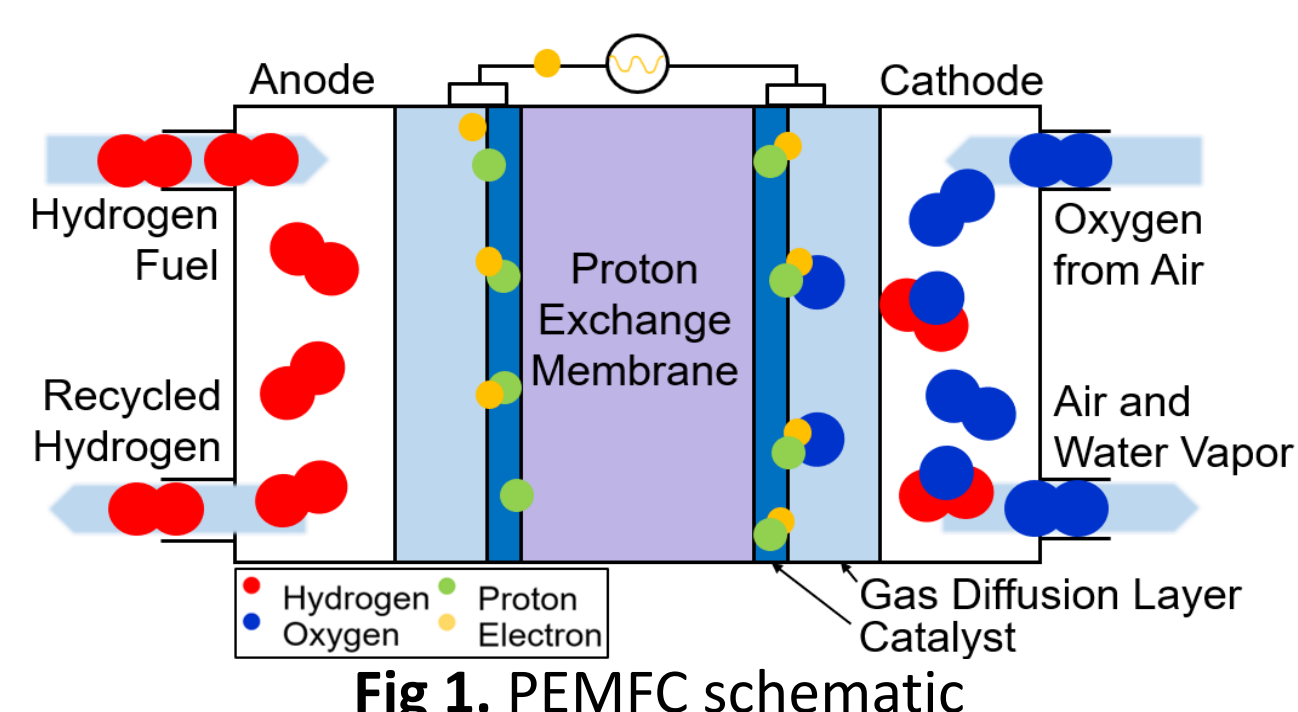


Fig 1. PEMFC schematic

Materials

Nafion: Perfluorosulfonic acid ionomer

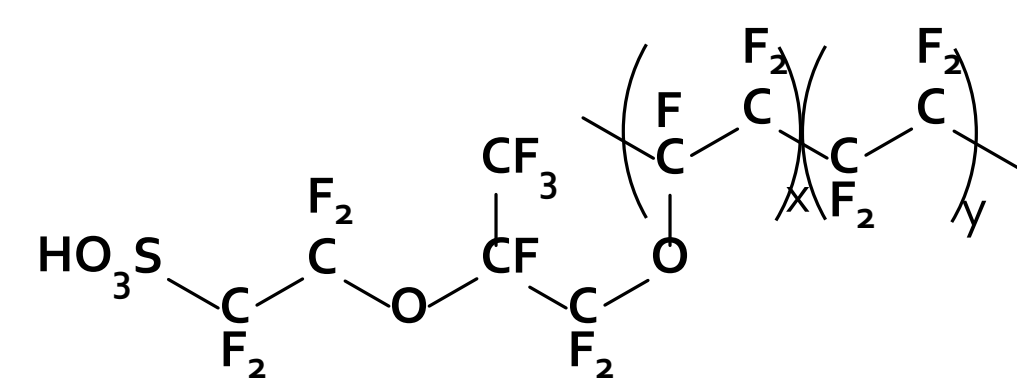


Fig 2. Chemical structure of Nafion

Methods

Sample Preparation

- Nafion solutions of varying wt % were sonicated for 20 min; spin-coated on Si wafer pieces; dried at 42°C for 3 h, annealed at 100°C for 7 h, cooled to room temperature under vacuum for 12 h.

Ellipsometry

- Film thickness values were obtained from ellipsometry

Contact Resonance Force Microscopy

- Oscillating current of increasing frequency in cantilever

Contact Resonance AFM (CRFM): Working Principle

CRFM with Relative Humidity Control

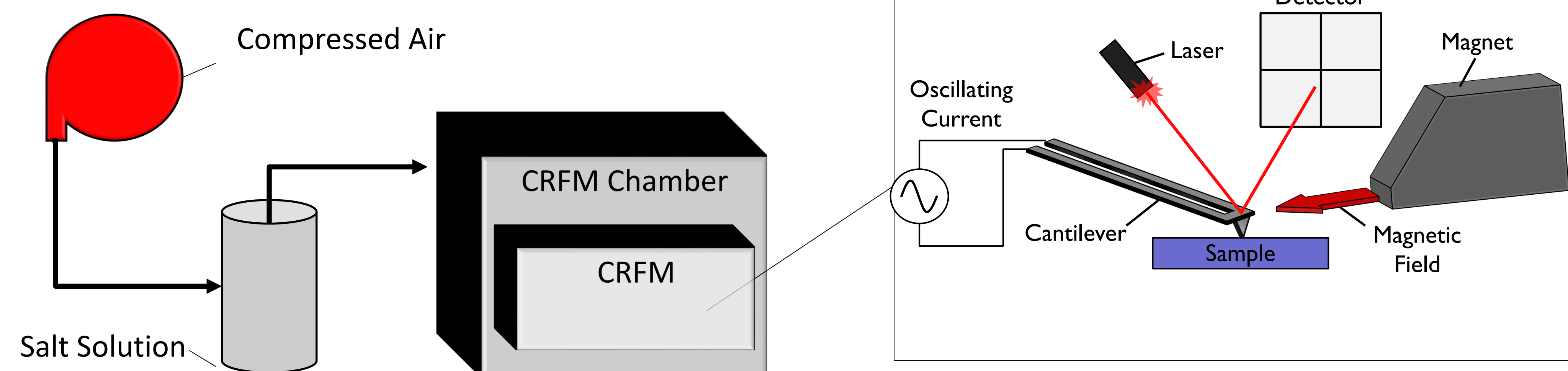


Fig 3. CRFM schematic with relative humidity control implemented

CRFM Measurements under controlled relative humidity

- Laser is reflected off a metallic cantilever
- Current causes cantilever to vibrate, laser records amplitude
- Vibrational modes appear as peaks in the amplitude curve
- Location and width of peak determine viscoelastic properties
- Compared against a bulk (80 μm) sample
- Saturated salt solutions will produce different **relative humidities**²
- Samples allowed to equilibrate for at least 10 h to absorb water from ambient air

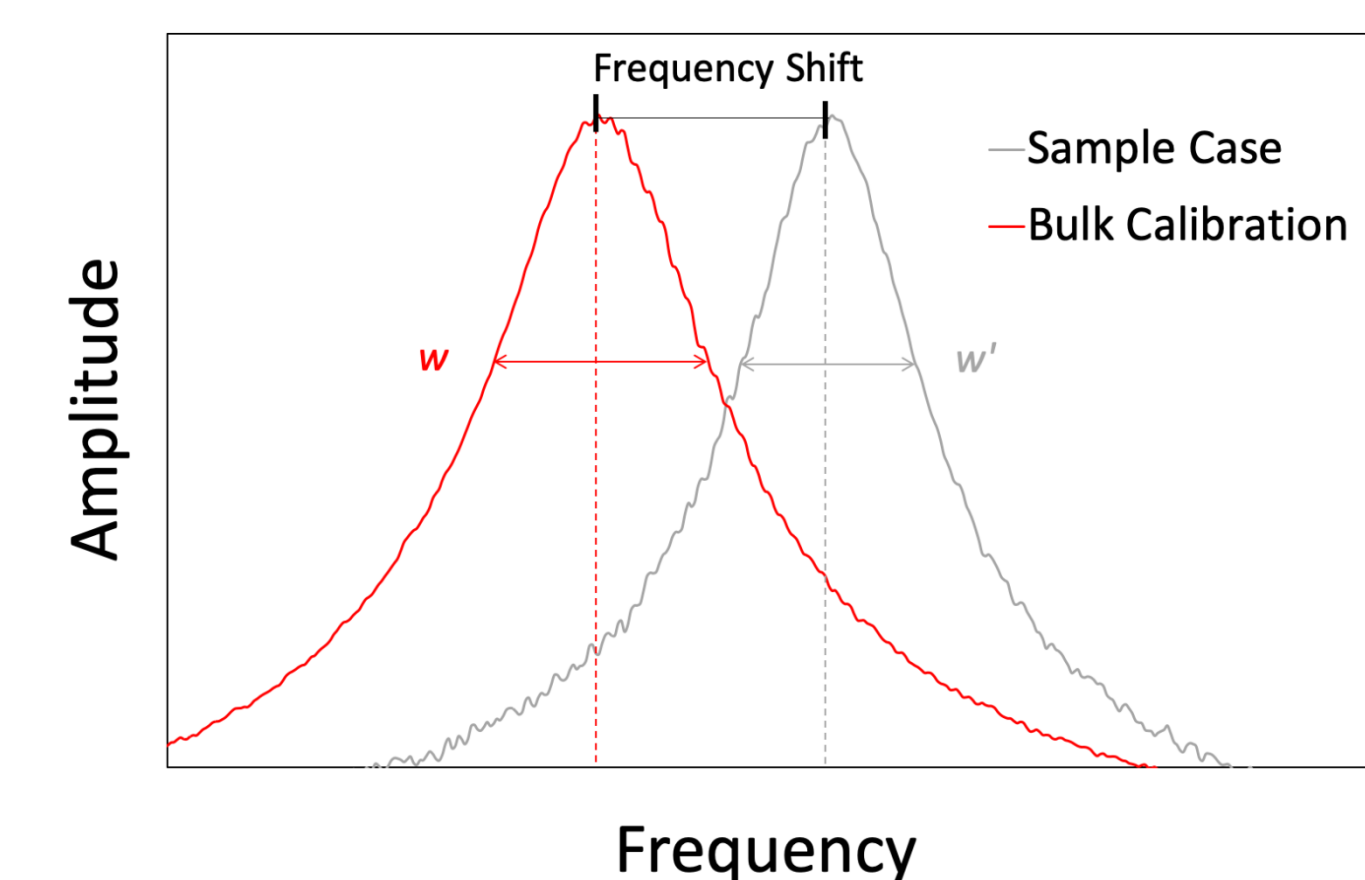


Fig 4. Example data

Results and Discussions

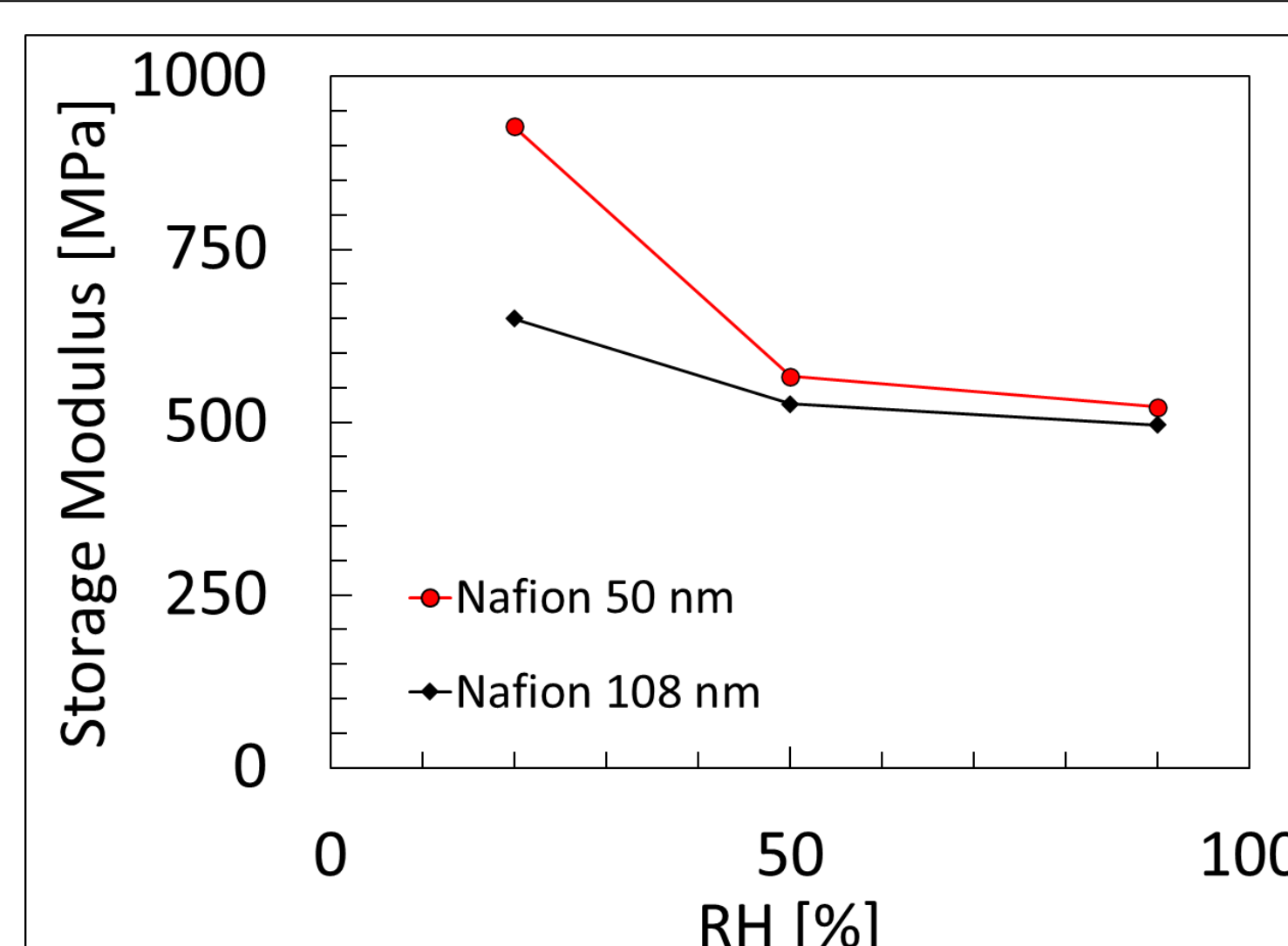


Fig 5. Storage Modulus of Nafion

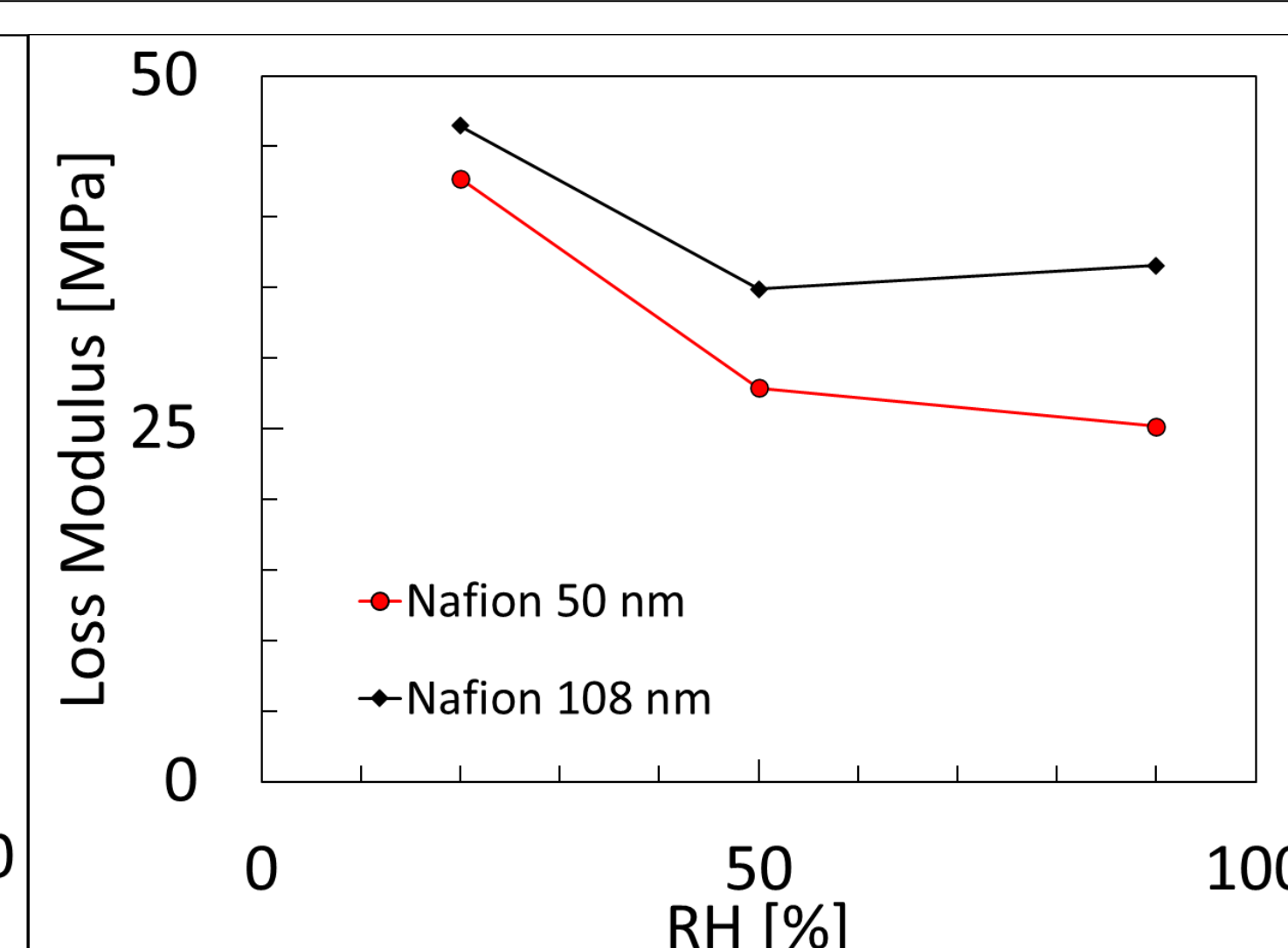


Fig 6. Loss modulus of Nafion

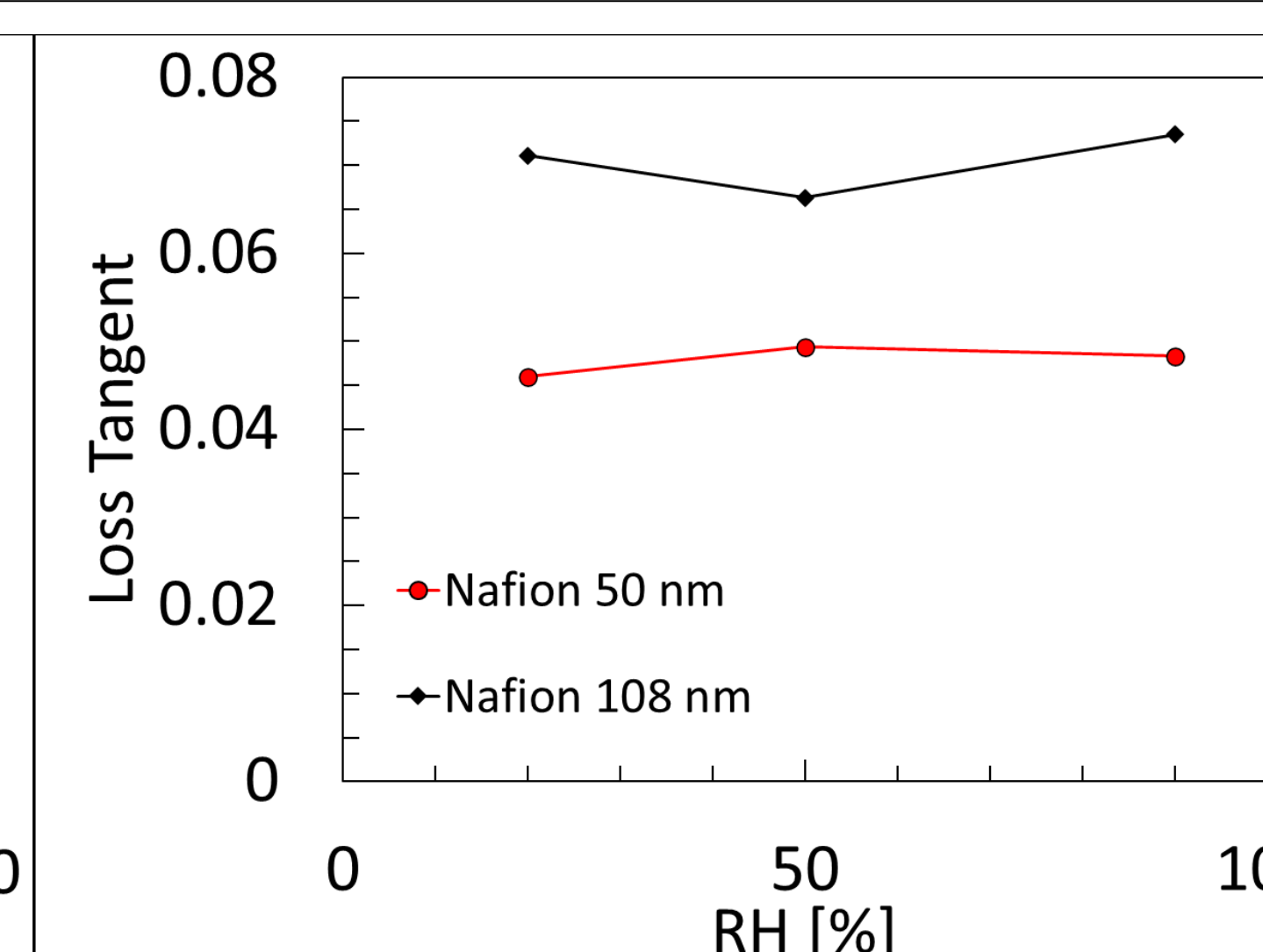


Fig 7. Ratio of viscoelastic properties of Nafion

Effect of humidity and film thickness on mechanical properties.

- At low relative humidity (~20%RH), films are much stiffer irrespective of the film thickness
- As the humidity went above ~20%RH, films started to plasticize or soften as can be seen from gradual decrease in storage and loss modulus. This was in agreement with our prior study of antiplasticization, followed by plasticization for Nafion thin films
- Thinner films are stiffer suggesting different polymer orientation and interaction with water and substrate

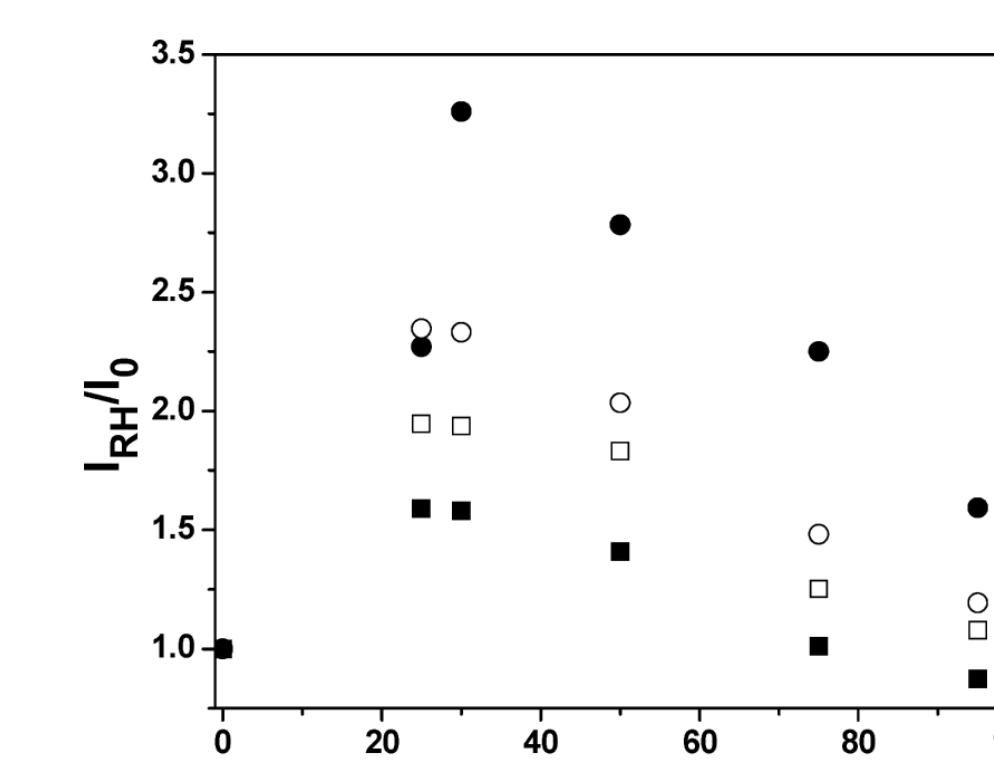


Fig 8. Relative fluorescence of Nafion films with thicknesses (■) 70, (□) 160, (○) 203, and (●) 616 nm⁴

Conclusions and Future Work

Film Properties and Relative Humidity

- Humidity based CRFM measurements are possible and confirm passed findings^{3,5}
- Viscoelastic properties are humidity dependent
- Increased side chain interactions and thinner films lead to less free volume and therefore more **confinement**⁶
- At low humidity, films become stiffer because of stronger interfacial interactions
- The stiffness of films can lead to poor conductivity

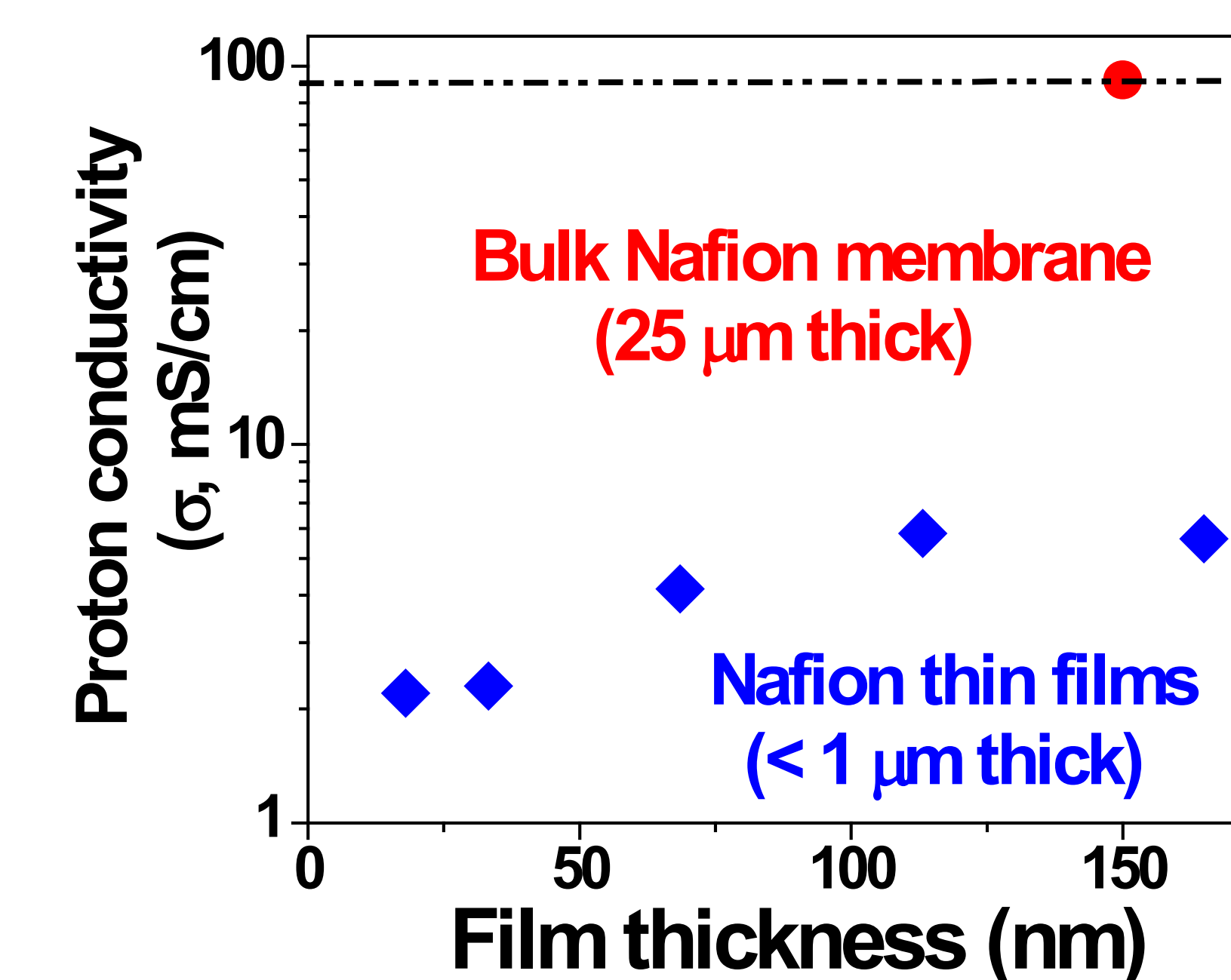


Fig 9. Conductivity data for Nafion

Future Work

- CRFM measurements will be expanded to more ionomers to develop larger framework of polymer knowledge
- Continue with samples of different thicknesses

References and Acknowledgments

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