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Nanomechanical Characterization of Fuel Cell Ionomers

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Introduction

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 PEMFCs[1]

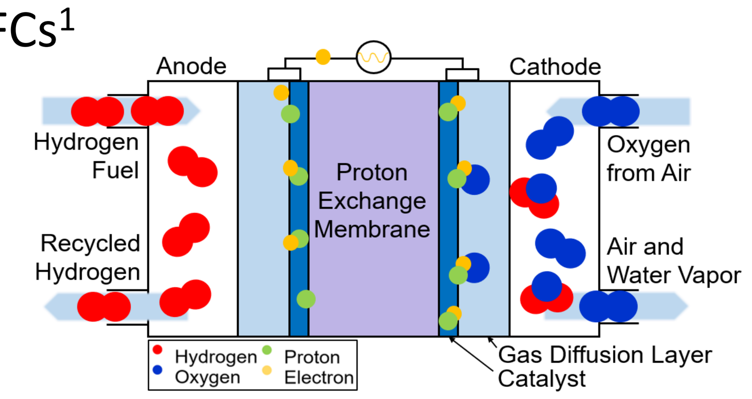

Fig 1. PEMFC schematic.

Materials

Nafion: Perfluorosulfonic acid ionomer

PFIA: Perfluoroimide acid ionomer

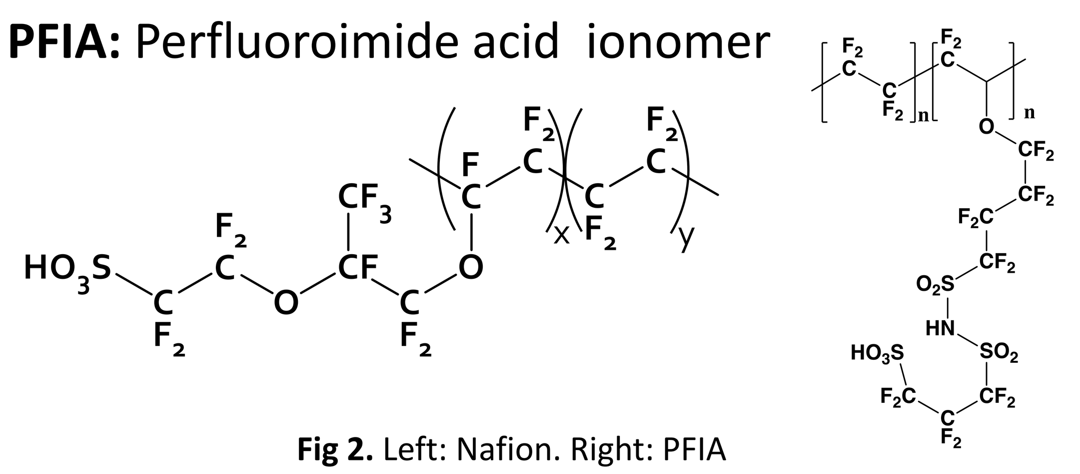

Fig 2. Left: Nafion. Right: PFIA

Methods

Sample Preparation

- Ionomer solutions (1, 2, 5, 7, 10 wt %) sonicated for 20 min; spin coated on Si wafer pieces; dried at 42°C for 3 hours then at 83°C for 7 hours; cooled in vacuum for 12 hours

Contact Resonance Force Microscopy

- Oscillating current of increasing frequency in cantilever

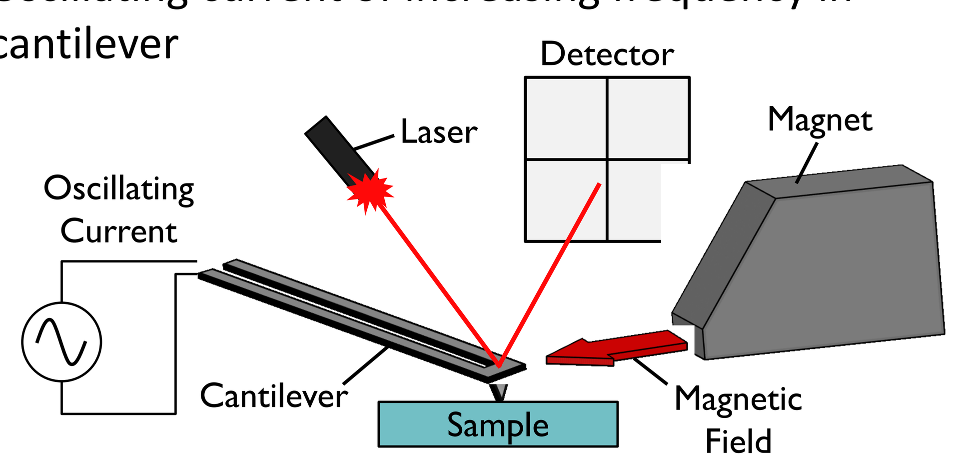

Fig 3. CRFM Schematic

Results

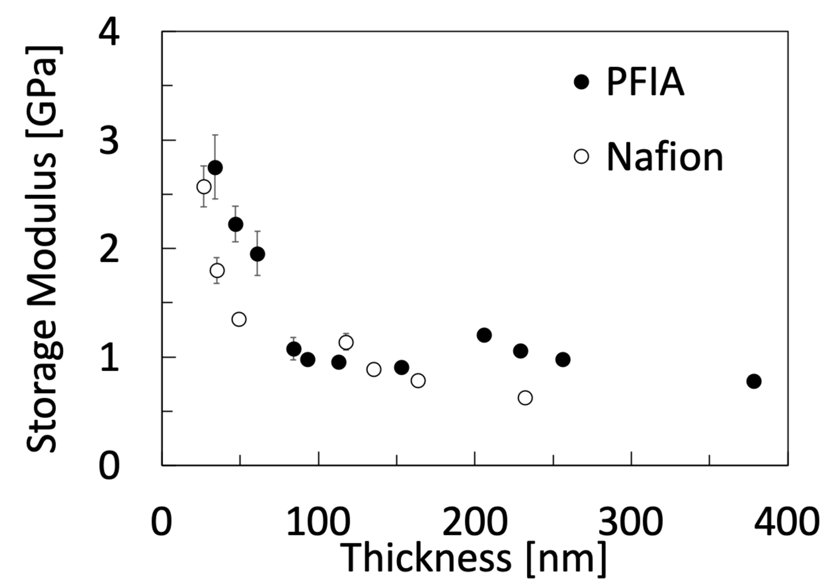

Fig 4. Stiffness of Nafion and PFIA

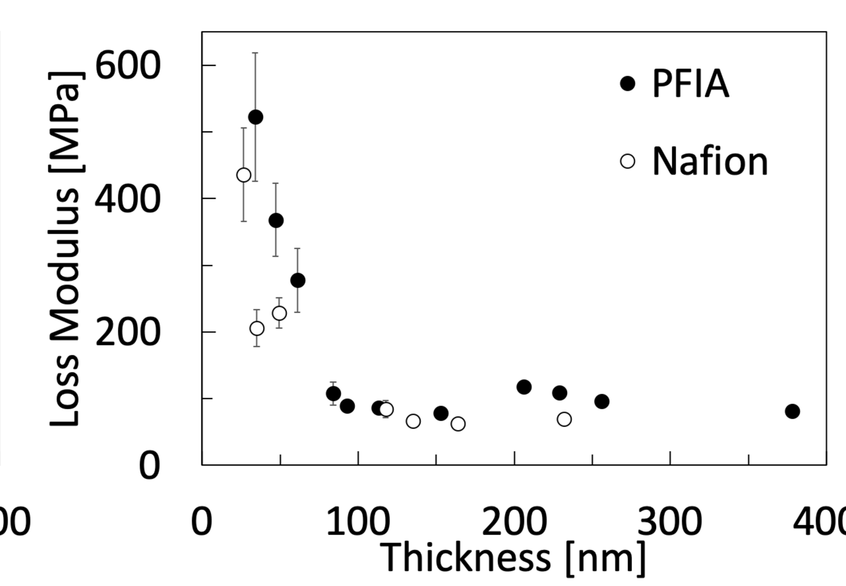

Fig 5. Loss modulus of Nafion and PFIA

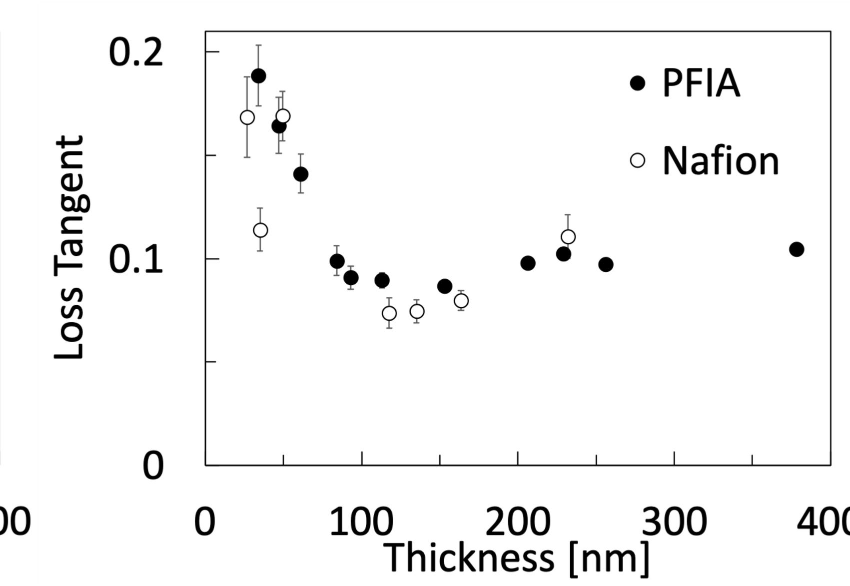

Fig 6. Ratio of viscoelastic properties of Nafion and PFIA

Comparison of Nafion and PFIA

- As the film thickness decreases, both storage and loss modulus increase.
- The small difference in viscoelastic modulus between these two ionomers suggests the insignificant impact of bisulfonyl imide group on viscoelastic modulus.

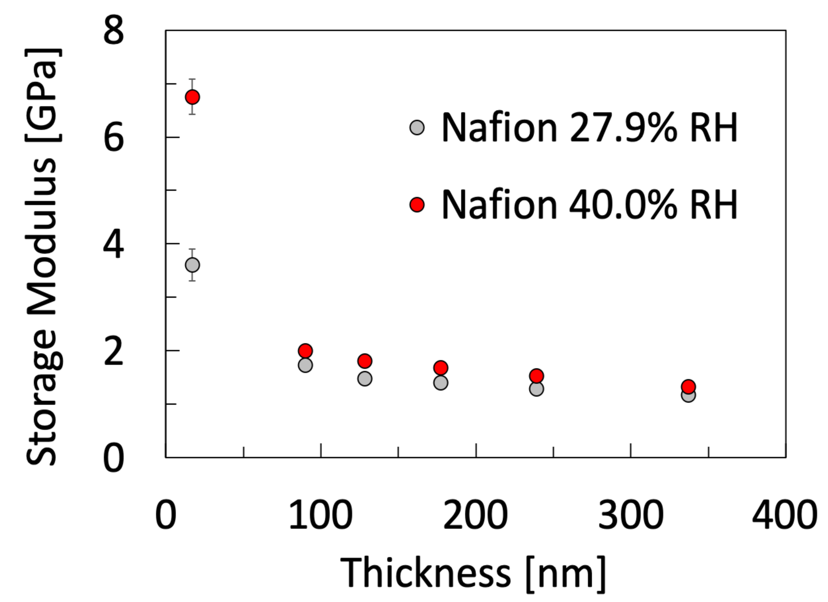

Fig 7. Effect of relative humidity on ionomer stiffness

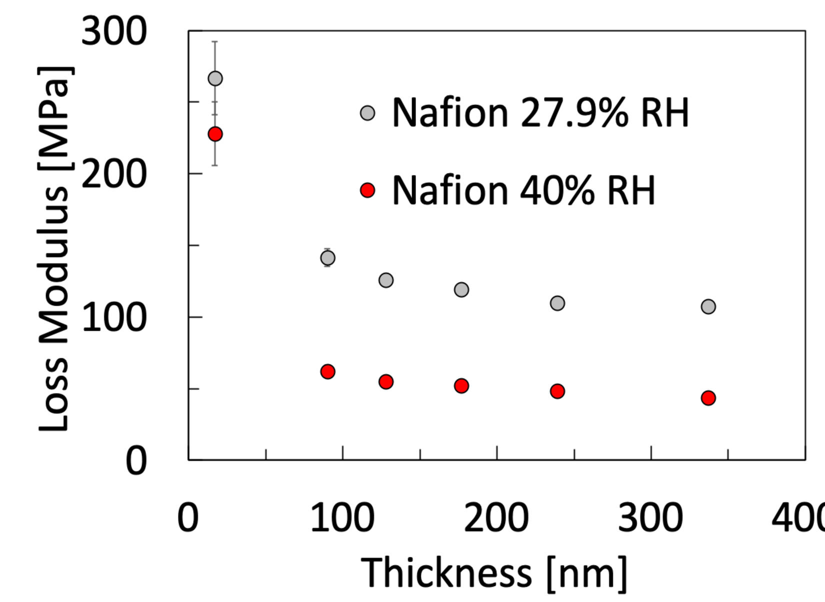

Fig 8. Effect of relative humidity on ionomer viscosity

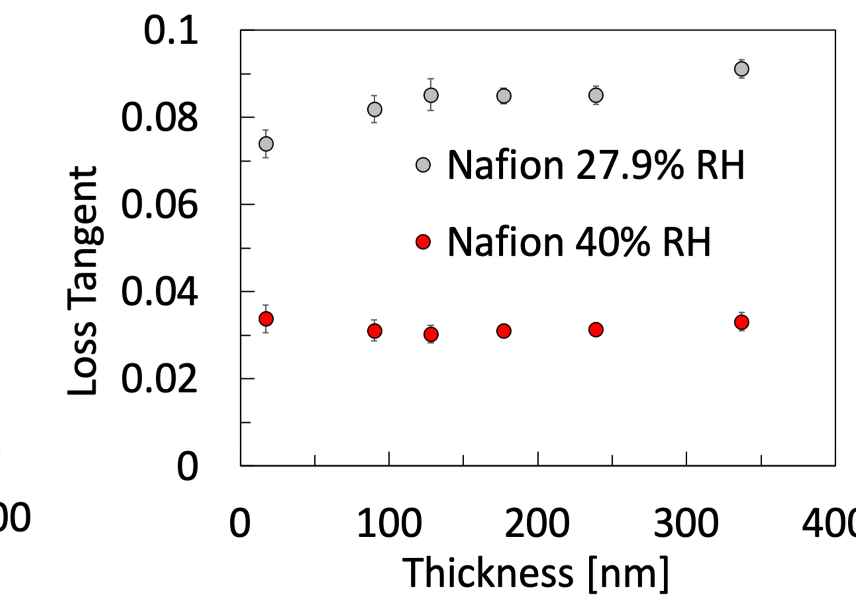

Fig 9. Ratio of viscoelastic properties under different relative humidities

Relative Humidity and Viscoelastic Properties

- *Increasing* the relative humidity *increases* stiffness when the film thickness is < 100 nm.
- At very low thickness, water and substrate both strongly *hydrogen-bond* with ionomer side chains and lead to a *drastic increase* in film stiffness.
- *Decrease* in loss modulus when % RH was increased from 28% to 40% is an interesting observation. This suggests *lower energy dissipation* with hydration.

Example of CRFM Data

- *Resonance frequency shift* related to storage modulus
- *Width* (*w*) is related to loss modulus
  - Free (no contact) case for *cantilever* properties
  - Nafion *bulk* (60 µm) for *film* calibration

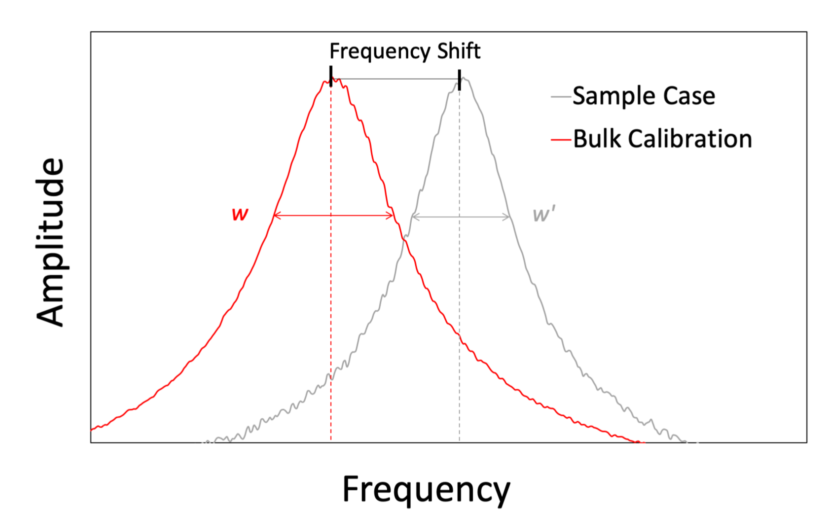

Fig 10. Example data

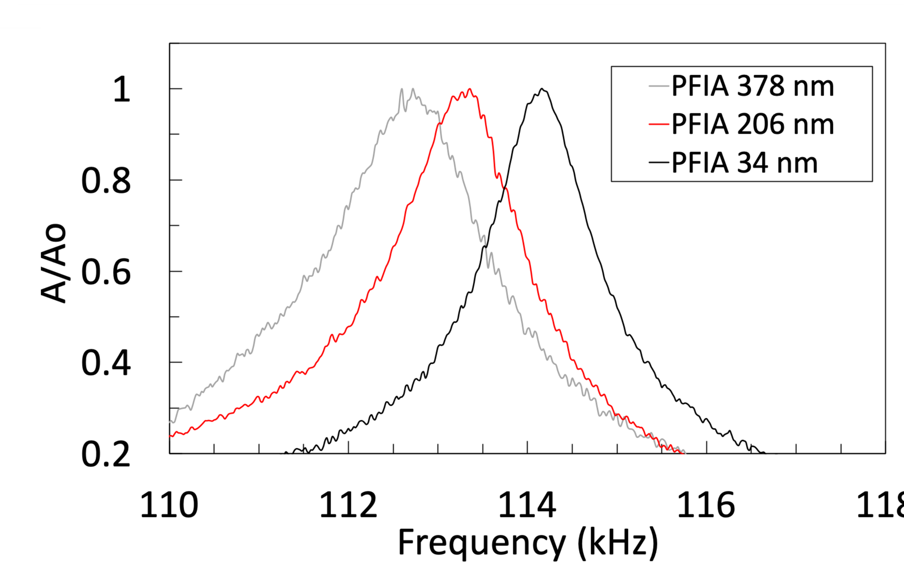

Fig 11. Sample of peaks used for measurements

Discussion

Film Properties and Thickness Effect

- In general, stiffness and viscosity increase as film thickness decreases below 100 nm[2,3]
- Increased side chain interactions and thinner films lead to less free volume and therefore more *confinement*[5]

Relative Humidity

- Relative humidity has a profound impact on viscoelastic properties[4]
- Water creates *strong* intermolecular forces due to highly polar side chains (hydrogen bonds)
- *Antiplasticization* occurs as %RH increased from 28% to 40%.

Conclusions and Future Work

Thin Film Polymers

- Storage and loss modulus increase as relative humidity increases and ionomer film thickness goes below 100 nm.
- In this specific study, the similar storage and loss modulus of Nafion and PFIA could be attributed to similar backbone structure and only slightly different flexibility of side chains.

Future Work

- Modify CRFM machine to create chamber to control *relative humidity*
- Implement Electrochemical Impedance Spectroscopy (EIS) to measure film *conductivity* in different relative humidities

References and Acknowledgments

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