Material Social Futures

LEVERHULME TRUST

Institute for Social Futures

Lancaster University

Extracting water states in thin proton-exchange membranes using terahertz time-domain spectroscopy

George A H Ludlam[1], Décio F Alves de Lima[1], Xiaoran Li[1], Bethan Coulson[2], Emily Nesling[2], Riccardo Degl'Innocenti[1], Richard Dawson[1], Massimo Peruffo[2], Hungyen Lin[1]

[1]Department of Engineering, Lancaster University, Lancaster, LA1 4YW, United Kingdom

[2]Johnson Matthey, Swindon, SN58AT, United Kingdom

Email: h.lin2@lancaster.ac.uk

2022 H2FC Supergen Research Conference

8th-9th June

Outline

1. **Introduction**
   - Motivation and aims
   - Molecular water states
   - Terahertz band and terahertz time-domain spectroscopy
2. **Materials and methods**
3. **Results**
   - Algorithm validation
   - Water retention and comparison to Dynamic vapor sorption
   - Extracted water states
4. **Summary**

Outline

1. **Introduction**
   - Motivation and aims
   - Molecular water states
   - Terahertz band and terahertz time-domain spectroscopy
2. **Materials and methods**
3. **Results**
   - Algorithm validation
   - Water retention and comparison to Dynamic vapor sorption
   - Water states
4. **Summary**

Introduction – Motivation and aims

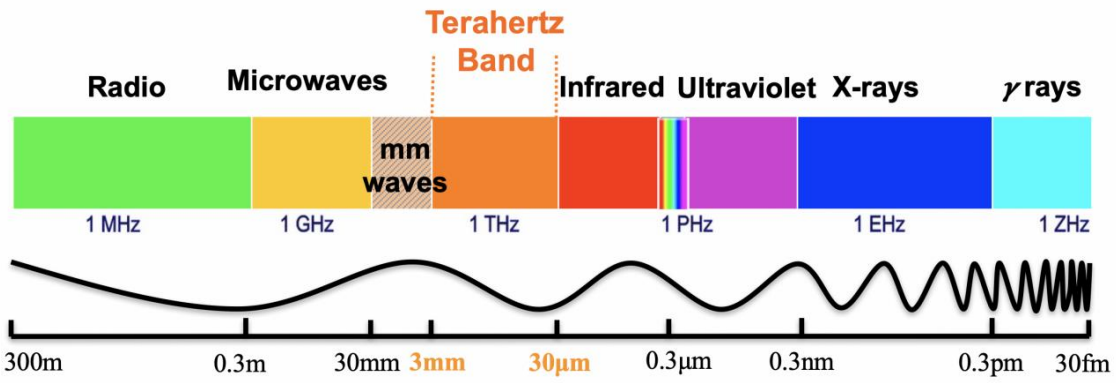
- **Motivation**
  - Membrane hydration
    - Proton conductivity
    - Swelling
  - Thin membranes
  - Heat treatments
  - Reinforcements
  - Additives/Fillers
- **Aims**
  - Develop an algorithm for analysis of water states in thin membranes using terahertz time-domain spectroscopy
  - Validation with previous work and complementary techniques

Introduction - Molecular water states

- **Bound**
  - Strongly bound with hydrogen bonds to the hydrophilic domain containing sulfonate groups
  - Very slow relaxation time
- **Bulk**
  - Weak temporary hydrogen bonds
  - Exhibits cooperative reorganization of hydrogen bonds
  - Associated with the formation of proton conducting channels
  - slow relaxation time
- **Free/Fast**
  - Not hydrogen bonded
  - Fast relaxation time
- Bulk and free water falls within terahertz dynamics

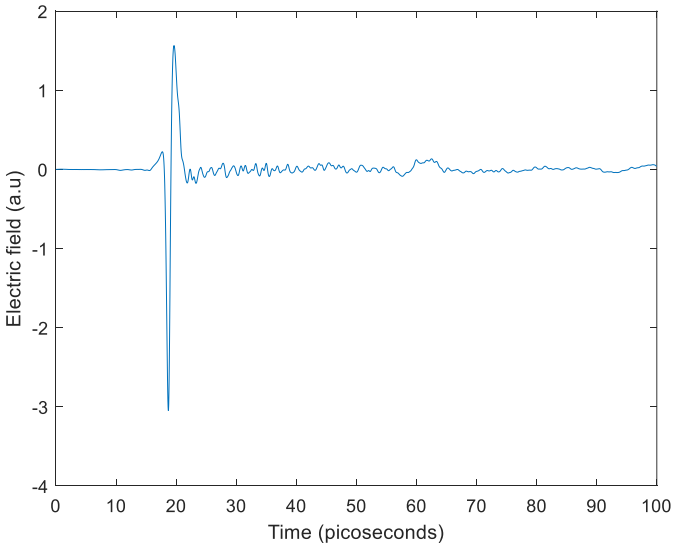
Introduction - Terahertz band

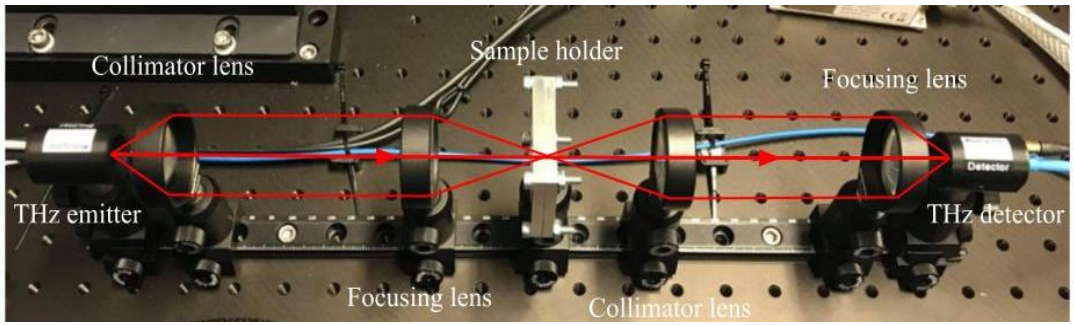
- Non-ionizing electromagnetic radiation
- Frequency range of 0.1-10 THz
- Bridges gap of electronics and photonics
- Material characterization
- Sensitive to structural thicknesses and chemical information
- Can penetrate many conventionally opaque, non-conductive materials



Introduction - Terahertz time-domain spectroscopy (THz-TDS)

- **THz-TDS**
  - Very short picosecond pulse measured in the time domain
  - Amplitude and phase of electric field measured
  - High signal to noise ratio
  - Non-invasive/destructive
  - Previously demonstrated for Nafion 117 [1],[2]





[1] N. Devi et al, Non-invasive macroscopic and molecular quantification of water in Nafion® and SPEEK Proton Exchange Membranes using terahertz spectroscopy, Journal of Membrane Science. 588 (2019).
[2] S.O. Yurchenko et al, Spectroscopy of nafion in terahertz frequency range, Journal of Applied Physics. 116 (2014).

Outline

1. **Introduction**
   - Motivation and aims
   - Molecular water states
   - Terahertz band and terahertz time-domain spectroscopy
2. **Materials and methods**
3. **Results**
   - Algorithm validation
   - Water retention and comparison to Dynamic vapor sorption
   - Water states
4. **Summary**

Materials and methods - Membrane preparation

- Commercial Nafion 117 membranes used for validation
- PFSA membranes prepared under different processing conditions by Johnson Matthey (13-70µm)
- Hydrated under 100% RH for 24 hours prior to THz-TDS measurement

Sample name	Ionomer	Thickness (µm)	Temperature and heat application	Duration	EEW (g/mol)
Nafion 117	N/A	160			N/A
Nafion 212	N/A	50			N/A
Nafion 211	N/A	25			N/A
Ionomer A1	A	13	Standard	Low	963
Ionomer A2	A	13	Standard	High	963
Ionomer A3	A	70	None		837
Ionomer A4	A	50	None		848
Ionomer A5	A	40	None		869
Ionomer A6	A	21	None		910
Ionomer B1	B	15	Low, New	Standard	963
Ionomer B2	B	15	Medium, New	Standard	963
Ionomer B3	B	15	High, New	Standard	963
Ionomer B4	B	15	Standard	Standard	963
Ionomer B5	B	15	Standard	Low	963
Ionomer B6	B	15	Standard	Very low	963

Materials and methods - Data analysis

- Fitting done using a parametric based algorithm developed in house [3]
- Determine thickness, total water content, bulk water fraction, free water fraction.
- Bound water fraction can be calculated from total water content, bulk water fraction and free water fraction

[3] D. F. Alves-Lima *et al.*, “Evaluation of water states in thin proton exchange membrane manufacturing using terahertz time-domain spectroscopy,” *Journal of Membrane Science*, vol. 647, p. 120329, Apr. 2022

Outline

1. **Introduction**
   - Motivation and aims
   - Molecular water states
   - Terahertz band and terahertz time-domain spectroscopy
2. **Materials and methods**
3. **Results**
   - Algorithm validation
   - Water retention and comparison to Dynamic vapor sorption
   - Water states
4. **Summary**

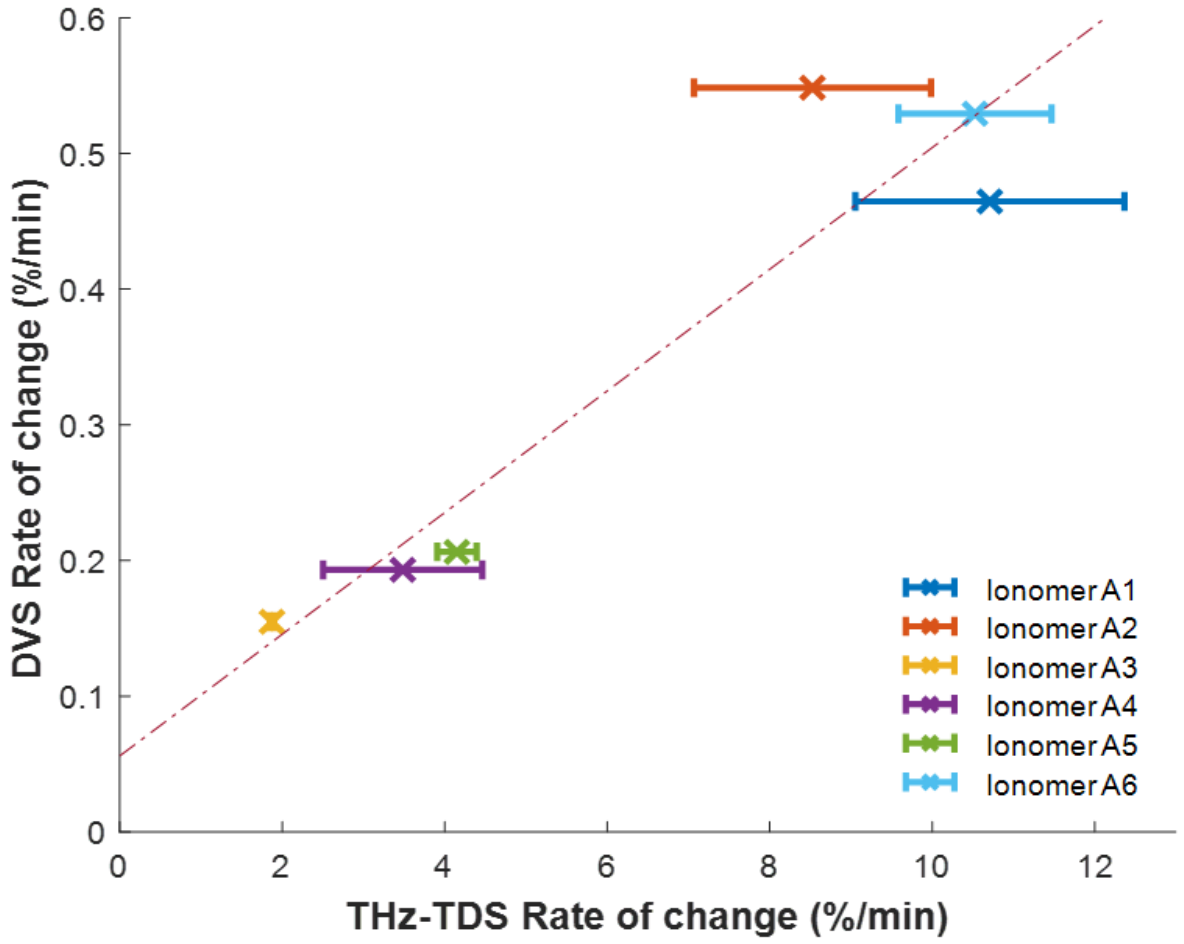
Results - Algorithm validation

- Membranes removed from 100% RH and placed in the ambient environment ~45% RH
- Validation against THz-TDS literature measurements for commercially available Nafion 117
- Extracted thickness consistent with measurements

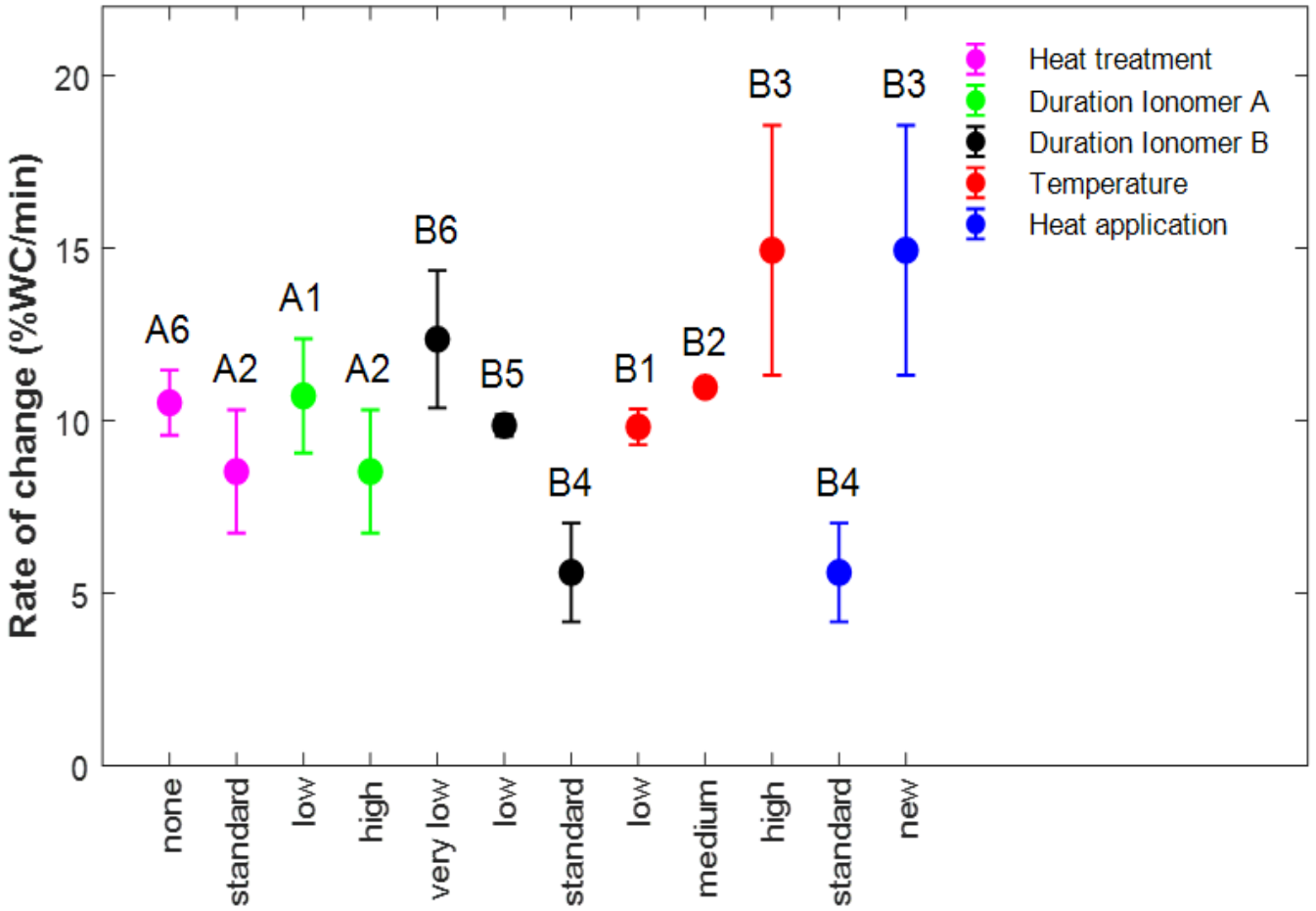
Initial water fraction	Literature [1]	Measurement
Bulk water	87.8%	86.5%
Free water	6.0%	4.6%
Bound water	6.2%	9.0%

[1] N. Devi et al, Non-invasive macroscopic and molecular quantification of water in Nafion® and SPEEK Proton Exchange Membranes using terahertz spectroscopy, Journal of Membrane Science. 588 (2019).

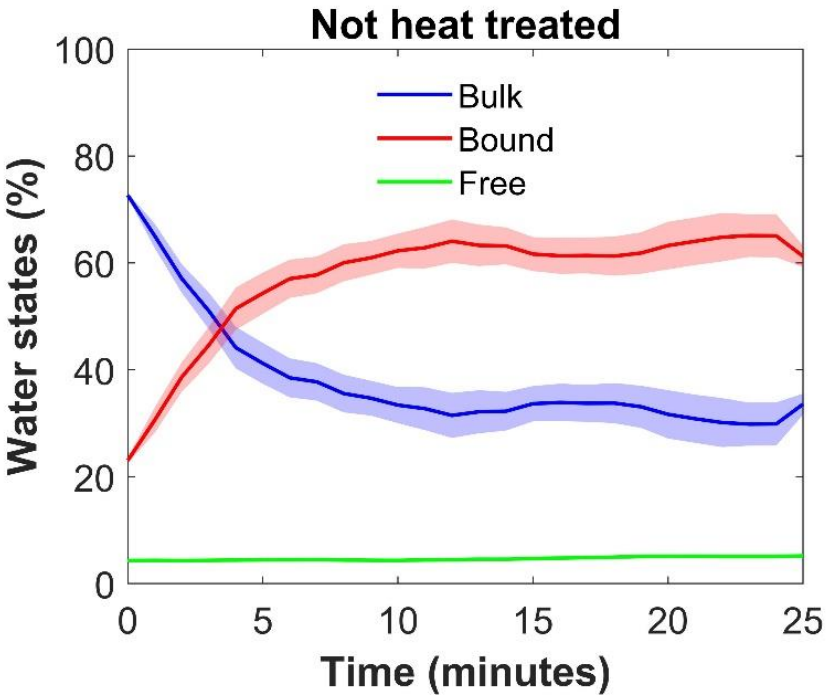
Results - Validation of water retention with DVS

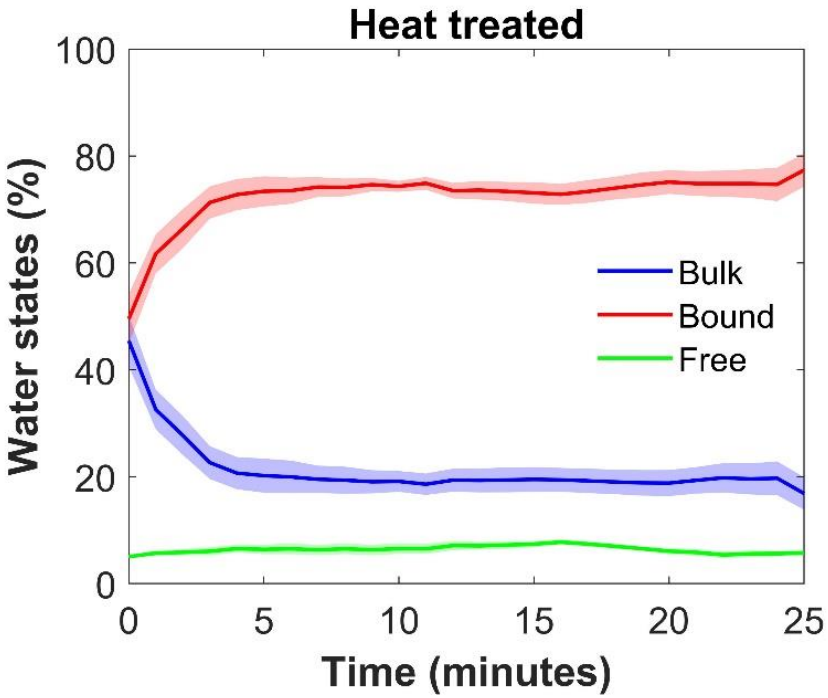


Results - Heat treatment strategy on water retention



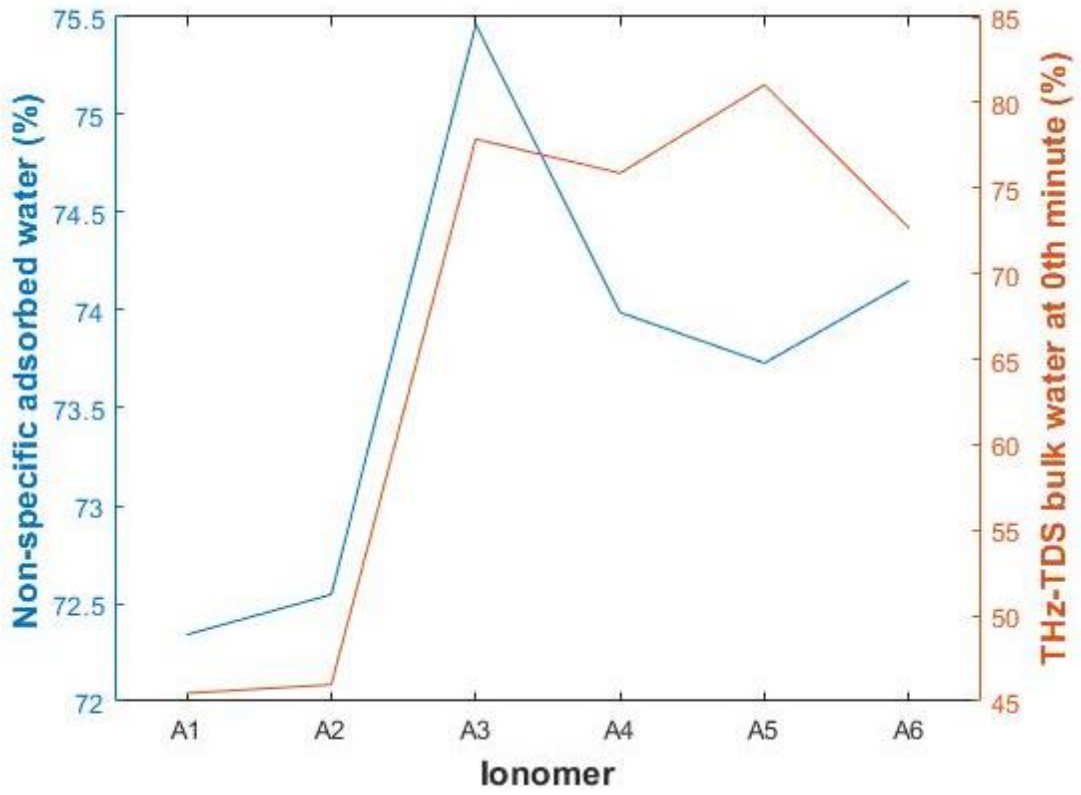
Results - Water states





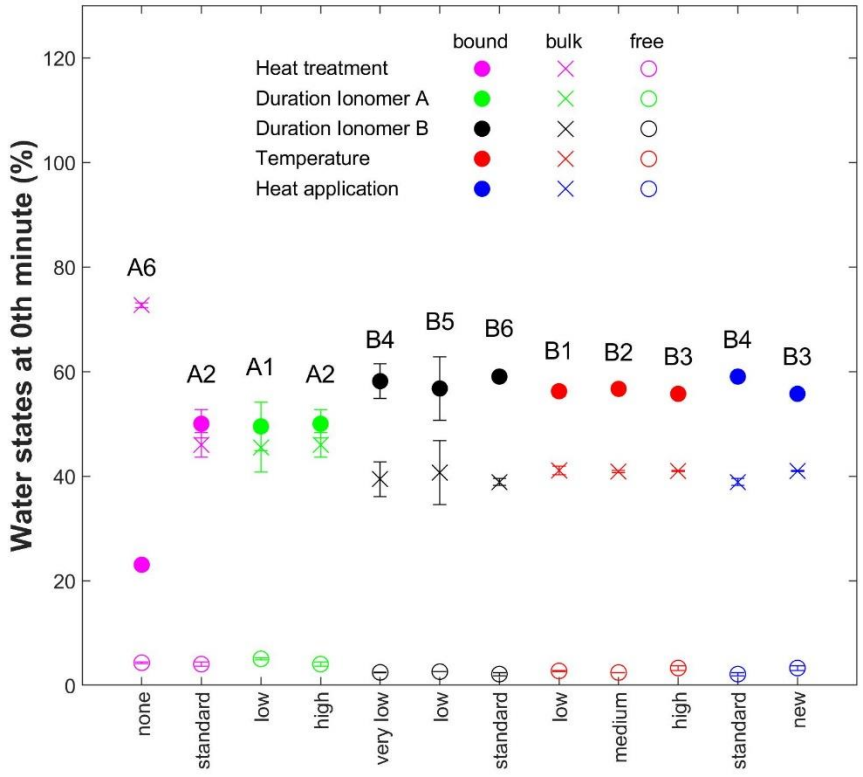
Results - Comparisons with DVS modelling

- **Adsorption isotherm fitting**
  - Henrys Law – non specific adsorbed water



Results - Heat treatment strategy effect on water states

- THz-TDS is sensitive to membranes prepared under different processing techniques
- Optimisation of mechanical and electrochemical performance



Outline

1. **Introduction**
   - Motivation and aims
   - Molecular water states
   - Terahertz band and terahertz time-domain spectroscopy
2. **Materials and methods**
3. **Results**
   - Algorithm validation
   - Water retention and comparison to Dynamic vapor sorption
   - Water states
4. **Summary**

Summary

- An algorithm has been developed for analysis of thin membranes using THz-TDS
- THz-TDS can be used as a method to quickly and non-invasive quantify water content in thin fuel cell membranes consistent with gravimetric techniques
- Sensitivity to both bulk and free water so all water states can be extracted
- Extracted water states can be used for rapid material characterisation with complementary techniques for optimisation and insights into material properties

Acknowledgements

- Johnson Matthey
- Financial support from the EPSRC (Grant No. EP/R019460/1, H2FC Supergen Flexible Grant EP/P024807/1)
- Leverhulme trust and the Materials social futures scholarship program

Material Social Futures

LEVERHULME TRUST

Institute for Social Futures

Lancaster University

Any questions?

George A H Ludlam[1], Décio F Alves de Lima[1], Xiaoran Li[1], Bethan Coulson[2], Emily Nesling[2], Riccardo Degl'Innocenti[1], Richard Dawson[1], Massimo Peruffo[2], Hungyen Lin[1]

[1]Department of Engineering, Lancaster University, Lancaster, LA1 4YW, United Kingdom

[2]Johnson Matthey, Swindon, SN58AT, United Kingdom

Email: h.lin2@lancaster.ac.uk

2022 H2FC Supergen Research Conference

8th-9th June