



Fabrication of ionic-liquid-based membranes for electrochemical devices

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Introduction

- Climate change is a significant threat to our planet, driving the need for cleaner, sustainable energy technologies like fuel cells.
- Nafion[®], a perfluorosulfonic acid polymer, has been the gold standard as a proton exchange membrane (PEM) for decades.
- However, Nafion[®] is expensive, environmentally persistent, and has poor performance at temperatures over 80 °C, prompting the search for alternative materials.

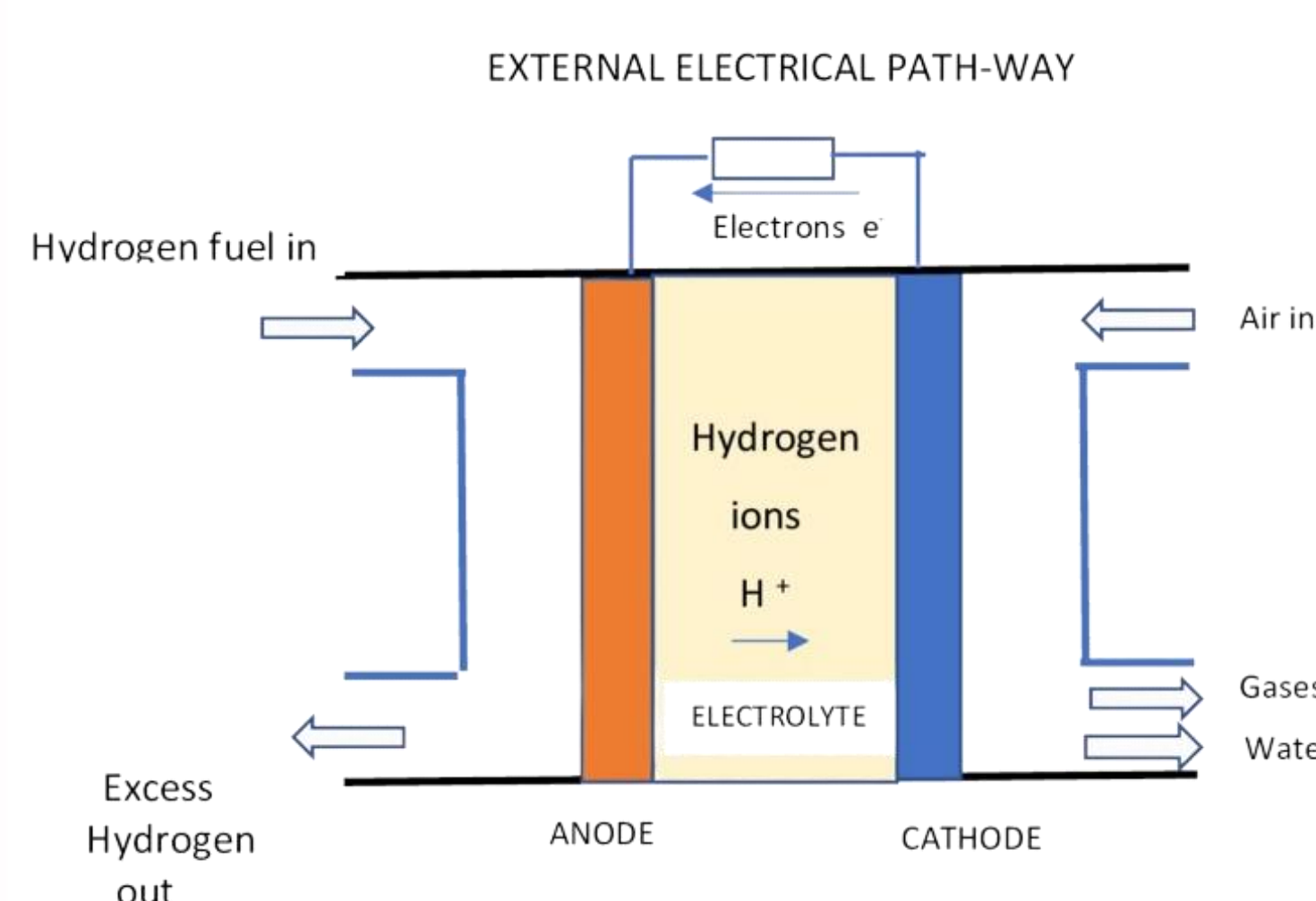


Fig 1. A schematic of a fuel cell

Requirements of a PEM:

- High proton conductivity
- Low electron conductivity
- High thermal stability
- Low gas permeability

Ionic-liquid-based alternatives:

- Nafion[®] + Protic ILs
- Polymerised Protic ILs
- Protic + Poly(IL) composite

Methodology

- This work explores protic + poly(IL) composite membranes inspired by the work of Rao *et al.*¹

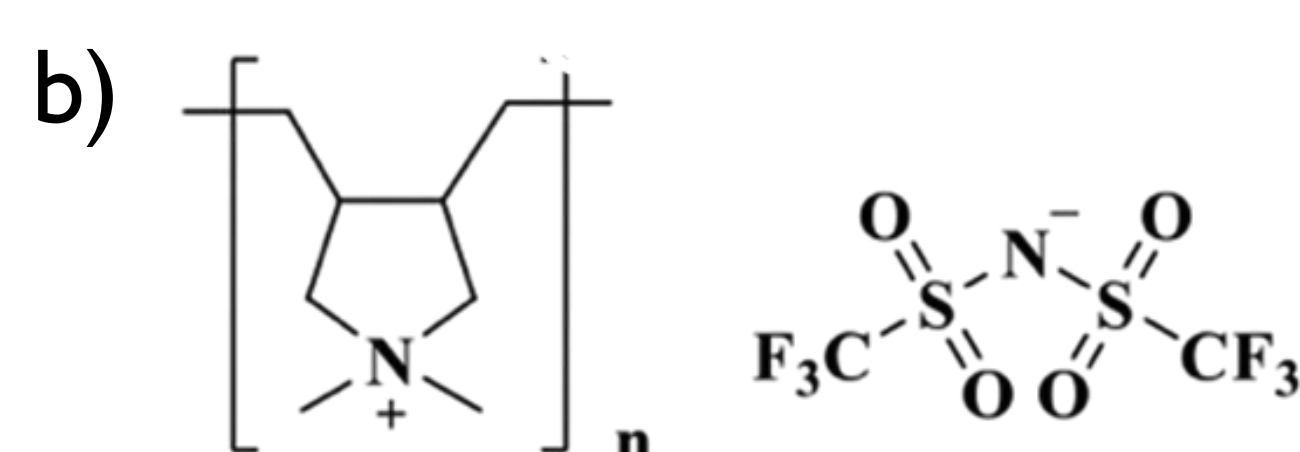
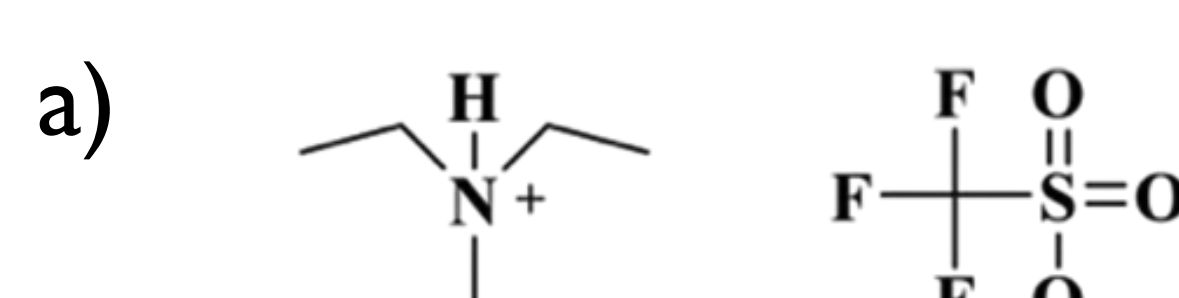


Fig 2. a) Protic IL [Hdema][TfO]

b) Poly(IL) [PDADMA][TFSI]

- Integration of protic IL, [Hdema][TfO], into a poly(IL), [PDADMA][TFSI], backbone.

- Examining various ratios to determine optimal PIL content

Synthesis

[Hdema][TfO]

- Acid-base neutralization (proton transfer) – N,N-diethylmethylamine + triflic acid
- Solvent and residual water removal – rotary evaporator and Schlenk line

[PDADMA][TFSI]

- Anion metathesis – PDADMAC + Li[TFSI]
- Filtering, washing with de-ionised water
- Drying – Schlenk line

Casting

- Solvent casting using MeCN in Ar glovebox



Fig 3. Casted composite membrane with 55 wt% PIL

References

[1] J. Rao *et al.*, "A novel proton conducting ionogel electrolyte based on poly(ionic liquids) and protic ionic liquid," *Electrochim Acta*, vol. 346, p. 136224, Jun. 2020, doi: 10.1016/j.electacta.2020.136224.

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Thermogravimetric analysis

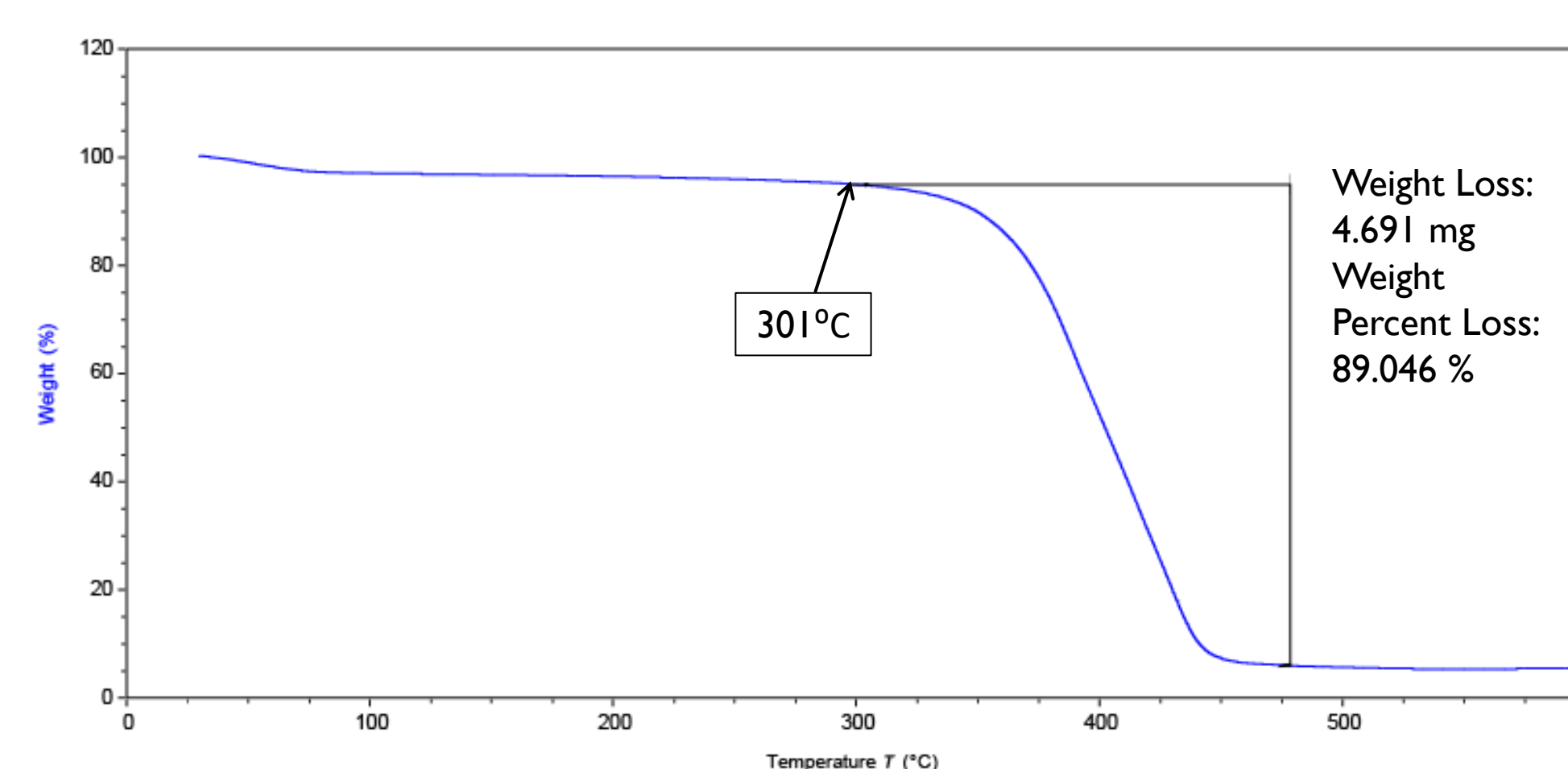


Fig 4. Example TGA plot of 55 wt% PIL membrane

Weight% of Protic IL	Average T _{decomposition}
45%	301 °C
50%	304 °C
55%	301 °C
60%	299 °C
65%	301 °C

Membranes casted at all ratios were found to have similar decomposition temperatures of *ca.* 300 °C

Table 1. Average membrane decomposition temperatures

Cyclic Voltammetry

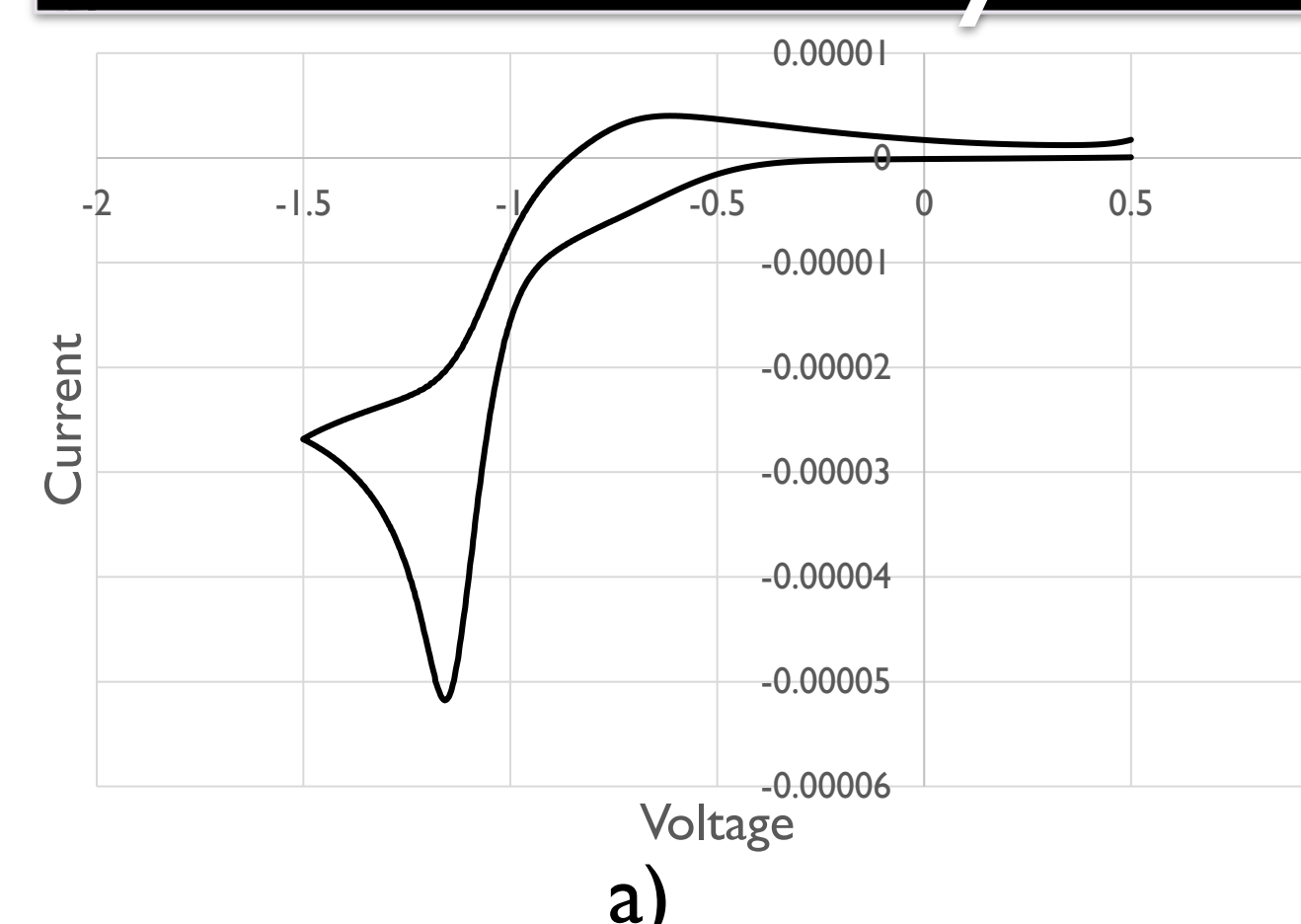


Fig 5. a) Cyclic voltammogram of [Hdema][TfO], b) Photo of 3-electrode set-up (Pt WE, Pt CE, Ag wire RE)

Cyclic voltammetry (at 100 mV s⁻¹) of [Hdema][TfO] shows the presence of labile protons, which should give conductivity of the membrane

ATR-FTIR

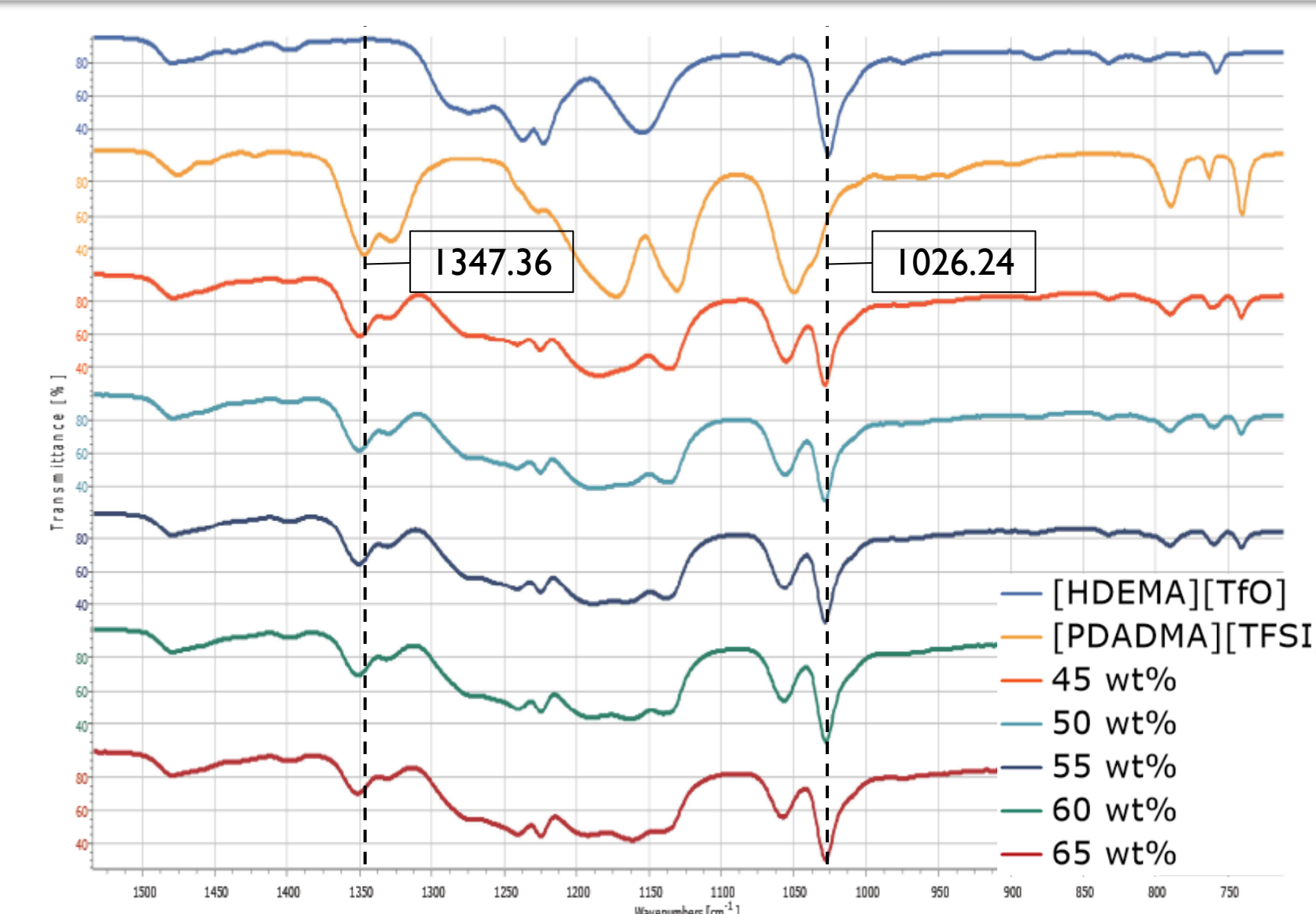


Fig 6. Example ATR-FTIR spectra

- Intensity increase for vibration at *ca.* 3064 cm⁻¹ (N-H group of PIL) as the PIL content increases
- 3 scans on 3 replicates of each PIL:poly(IL) ratio gave consistent FTIR fingerprint indicating homogeneously casted membranes.

Conclusion

Composite PIL:poly(IL) membranes at 45, 50, 55, 60 and 65 wt% were casted and showed similar thermal behaviour and chemical homogeneity. Further tests are required to explore their mechanical integrity and measure their ionic conductivity to assess their potential durability and performance for use in fuel cells.