

## Supplementary Information

### New molecular scale insights on the $\alpha$ -transition of Nafion® thin films from variable temperature ATR-FTIR spectroscopy

V. Ozhukil Kollath and K. Karan\*

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive, Calgary, AB T2N 1N4, Canada.

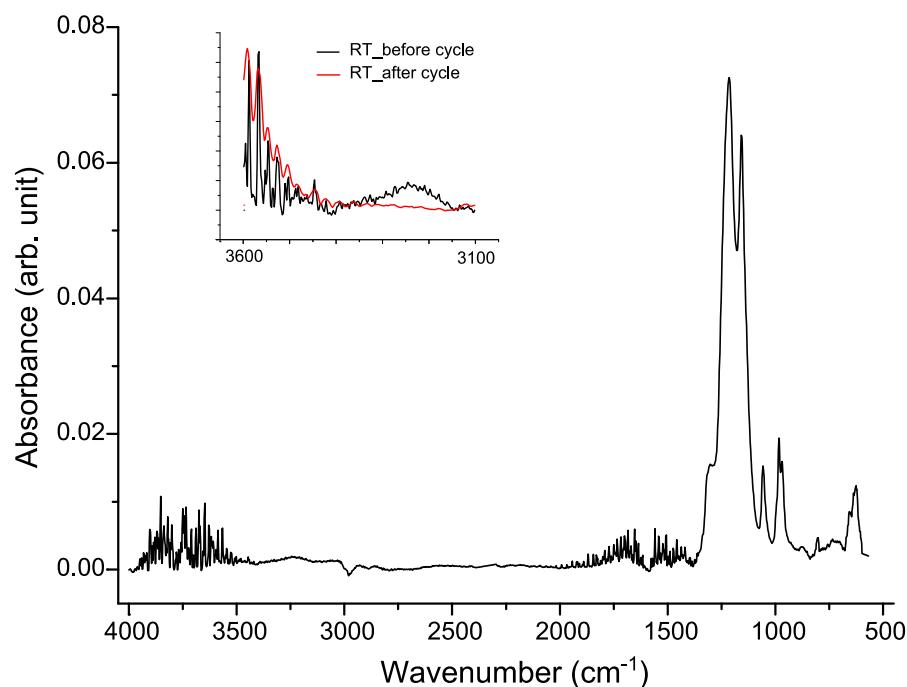


Fig. S1: Typical spectrum of vacuum dried Nafion film (80 nm). Inset shows the spectra comparison (3600 – 3100  $\text{cm}^{-1}$ ) recorded at room temperature (RT); before and after the first heating cycle.

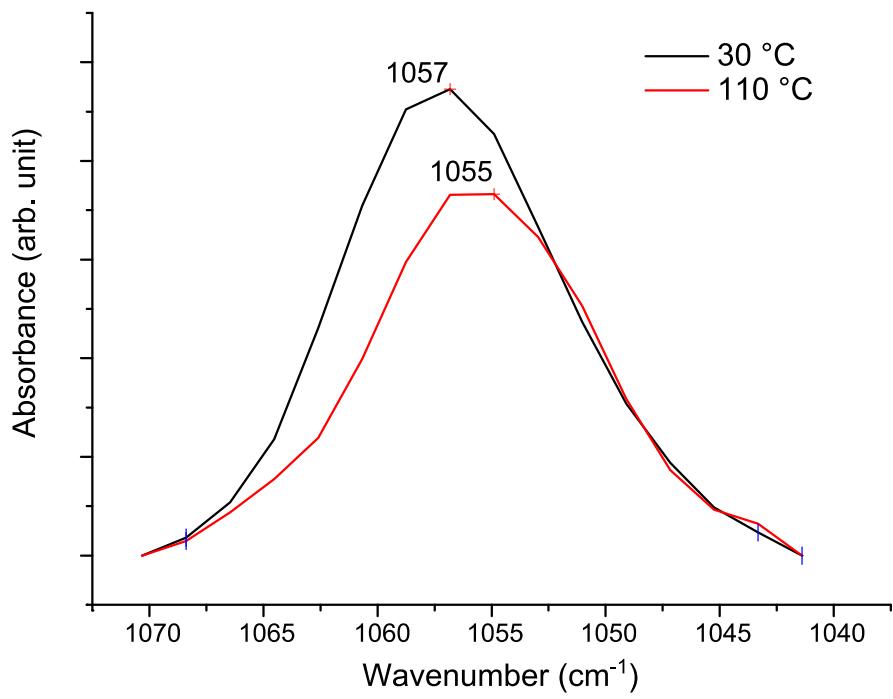


Fig. S2: Spectral region 1070 – 1040 cm<sup>-1</sup> for 26 nm Nafion film recorded at 30 °C (black) and at 110 °C (red).

---

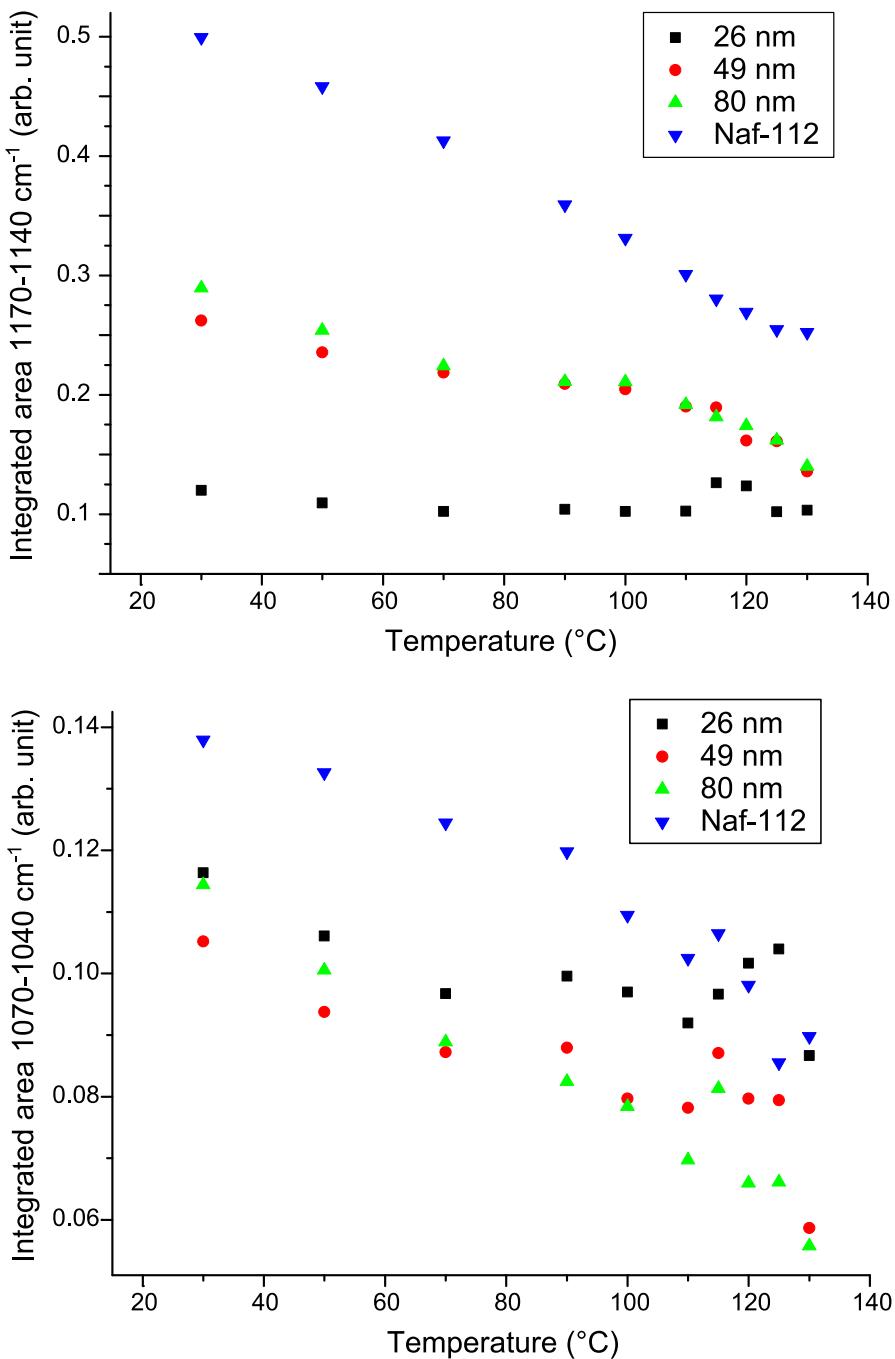


Fig. S3: Integrated area for the band  $1170 - 1140\text{ cm}^{-1}$  (top) and  $1070 - 1040\text{ cm}^{-1}$  (bottom), with respect to temperature for film thicknesses 26 nm, 49 nm, 80 nm and commercial Nafion® 112.

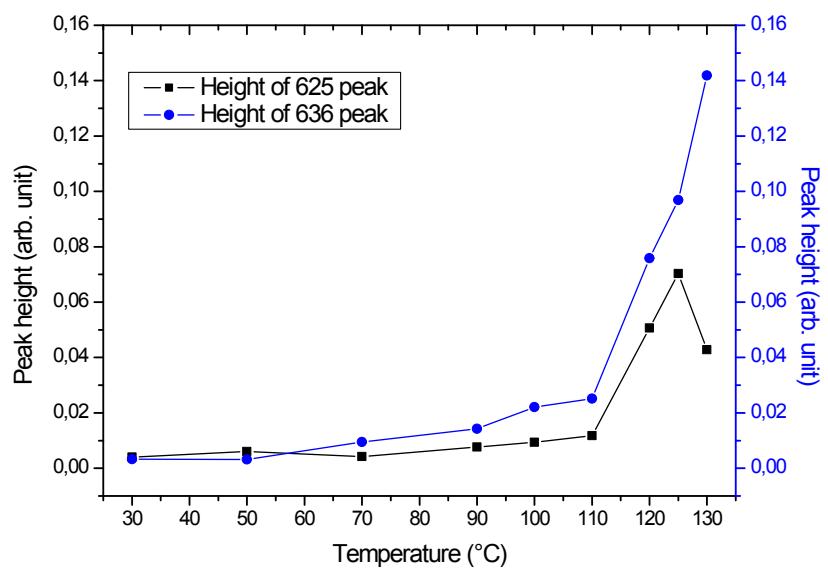
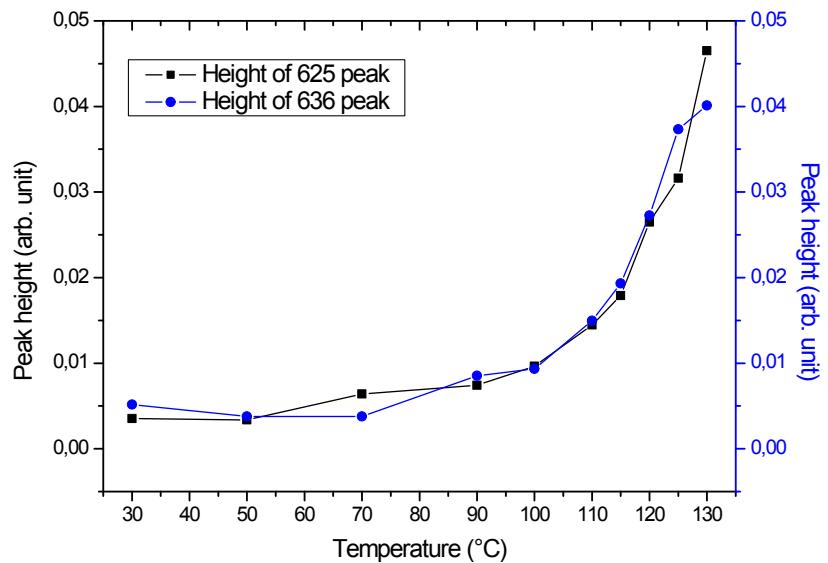


Fig. S4: Peak heights of bands at 636 and 625  $\text{cm}^{-1}$  from the doublet region 655-615  $\text{cm}^{-1}$  for (a) PTFE membrane and (b) 26 nm Nafion film.

### Peak fitting method:

The results shown below (fig. S5) are obtained by applying an automatic multi-peaks Gaussian fit function to the band 650-615 cm<sup>-1</sup> band using Origin 7.0 (OriginLab Corporation).

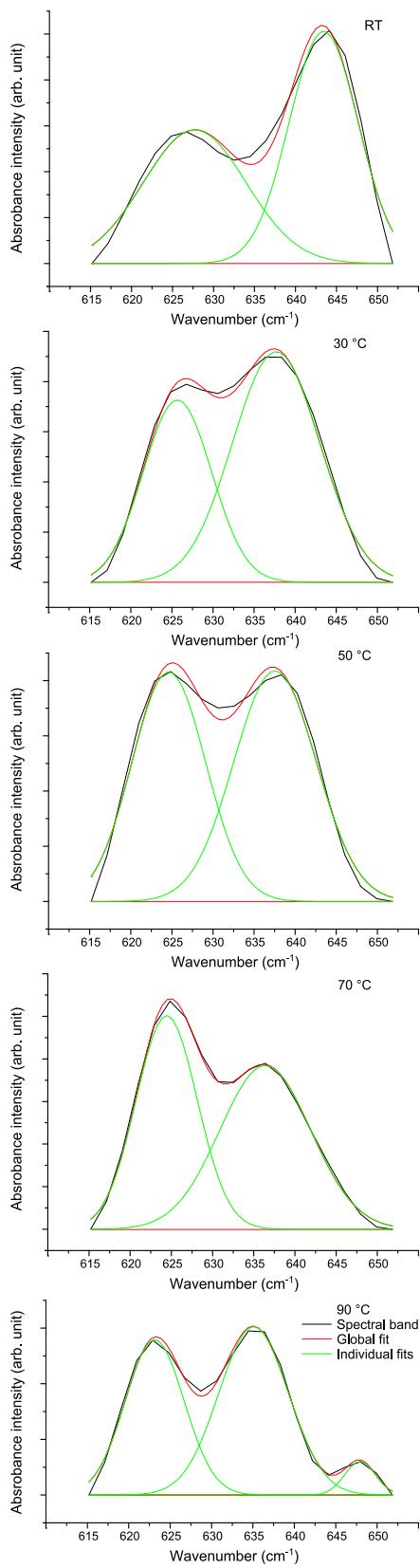


Fig. S5: Peak fitting results for the 636-624 cm<sup>-1</sup> doublet in the PTFE membrane at RT, 30, 50, 70 and 90 °C.

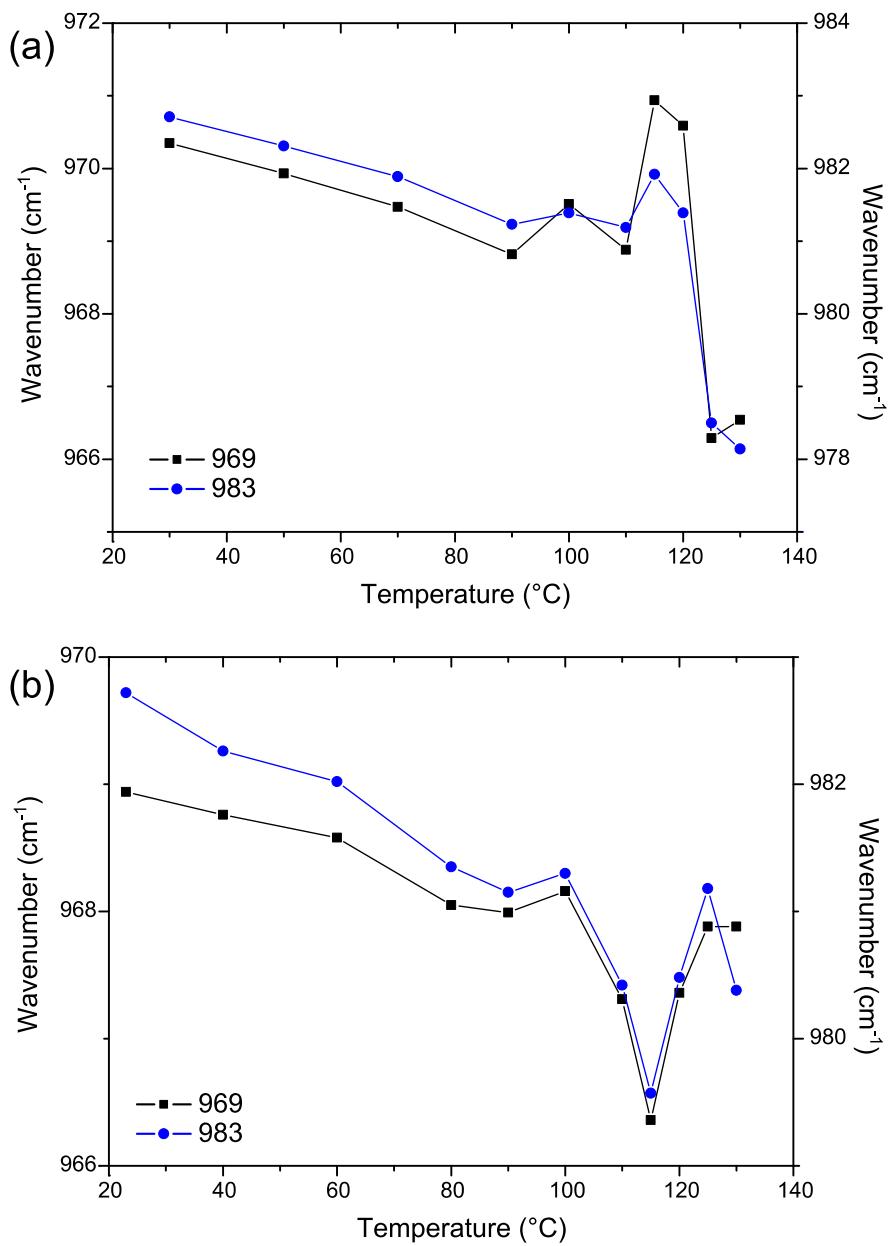


Fig. S6: Graphs show the change in respective peak position with respect to temperature, for (a) 26 nm and (b) 80 nm films.