Quantifying humidity dependent water states of Nafion 117 membranes using terahertz time-domain spectroscopy

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Abstract: Terahertz time-domain spectroscopy has been used to extract the water states of proton exchange membranes prepared at different relative humidities using saturated salt solutions and the results obtained show good agreement with literature.

1. Introduction

Proton exchange membranes are semi-permeable membranes designed to selectively conduct protons via water while acting as a barrier for electrons and reactant gases. These membranes are used inside electrochemical devices such as fuel cells and electrolyzers. Performance of these membranes is highly dependent on the amount of water in the membrane itself, which generally exist within 3 states: bound water (strongly hydrogen bonded), bulk water (weakly hydrogen bonded and exhibiting co-operative reorganisation of hydrogen bonds) and free water (not hydrogen bonded) [1, 2], where bulk water facilitates proton conduction via the Grotthuss mechanism. As proton conductivity is directly related to performance, extracting water states is therefore important for the optimisation of these products. We have previously demonstrated how terahertz time-domain spectroscopy (THz-TDS) can be used to extract water states inside industrially relevant membranes at the fully hydrated condition [1]. To better understand how these membranes behave at different levels of hydration, here we build on our earlier demonstration to analyse membranes prepared at different hydrations using saturated salt solutions.

2. Methodology

Nafion 117 membranes (183µm thick) were prepared into 3x3 cm squares which were cleaned and activated at 80 °C using 3%H_2O_2 followed by 0.5M H_2SO_4 for 1hr. The membranes were then hydrated at different relative humidities using the saturated salt solutions shown in Table 1 for 24 hours. THz-TDS measurements of hydrated membranes were taken using a TERA K15 spectrometer (Menlo Systems, Germany) in free space under ambient conditions. An in-house developed parametric based algorithm was used to perform the analysis of the acquired waveforms to extract the water states [1].

3. Results

Fig. 1 shows a good agreement between our extracted complex permittivity values against previous work [2,3], highlighting the reproducibility of the data. We then compared our extracted water contents with gravimetric based dynamic vapor sorption from literature [4] where a good agreement was seen as shown in Table 1.

Table 1. Saturated salt solutions

Saturated salt	Measured relative humidity (%)	Measured water content (wt%)	Literature water content (wt%) [4]
$MgCl_2$	38-40	7.7±0.2	7.7
K_2CO_3	47	9.5	8.6
NaCl	74-78	13.7±0.2	13.1
DI water	100	24.0±0.4	26.0

From our measurements, we then calculated their water states as shown in Fig. 2. Based on these results, we can observe an increase in the proportion of bulk water over bound with increasing hydration levels consistent with previous work [5].

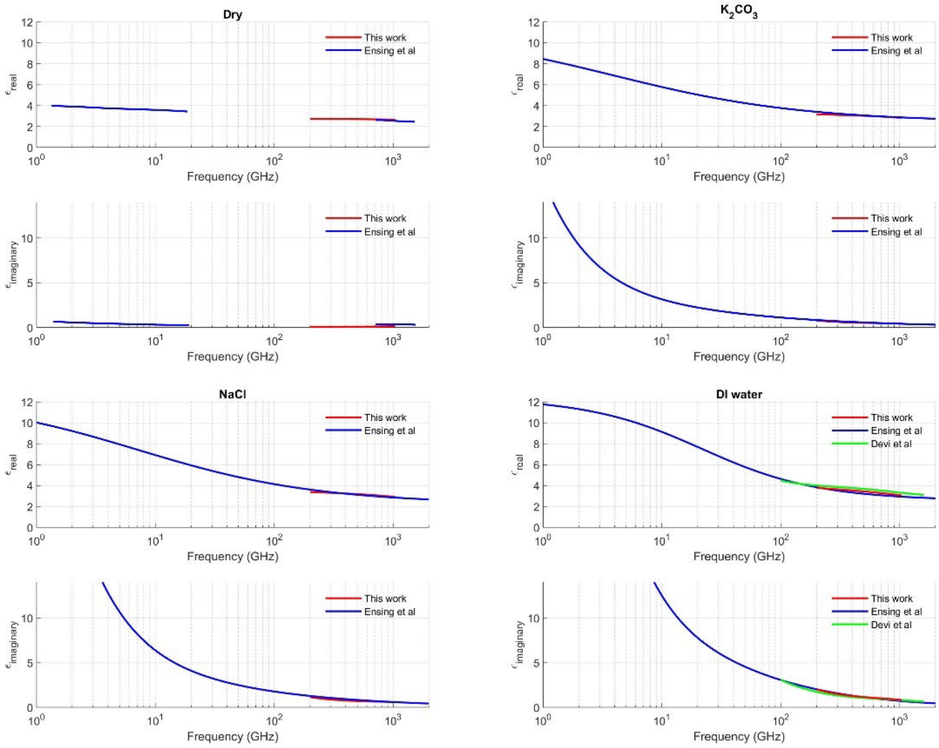

Fig. 1. Complex permittivity of Nafion 117 fittings compared with literature THz-TDS [3] and microwave dielectric spectroscopy fitted to the Cole-Cole model [2].

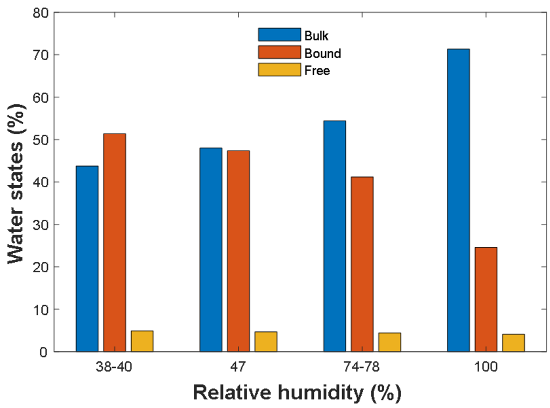

Fig. 2. Water states of Nafion 117 at different humidities.

4. Conclusion

In this work, we have characterized the dielectric properties, water contents and states of Nafion 117 prepared at different hydrations using THz-TDS producing results consistent with previous reported values. These results highlight the potential of this table-top technique for rapid product testing and optimizations.

5. Acknowledgements

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6. References

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