Quantification of water states in thin proton exchange membrane manufacturing using terahertz time-domain spectroscopy

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***Abstract*—Water states in proton exchange membranes have previously been extracted using terahertz time-domain spectroscopy (THz-TDS) for thick Nafion membranes. In this work, we have developed a parametric based algorithm for data analysis and applied it to thin industrially relevant membranes (13-70µm), processed under different conditions, producing results consistent with conventional gravimetric analysis and prior demonstrations. This therefore opens up opportunities for rapid membrane investigations and understanding.**

I. INTRODUCTION

PROTON exchange membrane fuel cells (PEMFCs) are electrochemical devices for clean conversion of hydrogen to electric energy. Proton exchange membranes conduct protons via water between the catalyst layers while providing a barrier for reactant gases and electrons. 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, which is directly related to performance. THz has quickly been gaining popularity for material characterisation [3-7] and THz-TDS has been shown to resolve water states of these membranes at thickness of ~170 µm non-invasively [1]. Here we build on the technique to include industrially relevant thin membranes at 13-70 µm [2].

II. METHODOLOGY

Membranes at thicknesses of 13-70 µm (Johnson Matthey, UK) were prepared under different heat treatments strategies as summarised in table 1.

Parameter	Range
Heat treatment	None and Standard
Duration of heat treatment	High, Standard, Low and Very low
Temperature of heat treatment	Low, Medium and High
Heat application	Standard and New

Table 1. Comparison of maximum desorption rate between THz-TDS and DVS

Membranes were hydrated at 100% relative humidity inside a home-built humidity chamber for 24 hours prior to THz-TDS measurements (TERA K15, Menlo Systems, Germany) in free-space with ambient conditions for a period of 15 minutes. Analysis of the acquired waveforms was then performed using an in-house developed parametric-based algorithm [2].

III. RESULTS

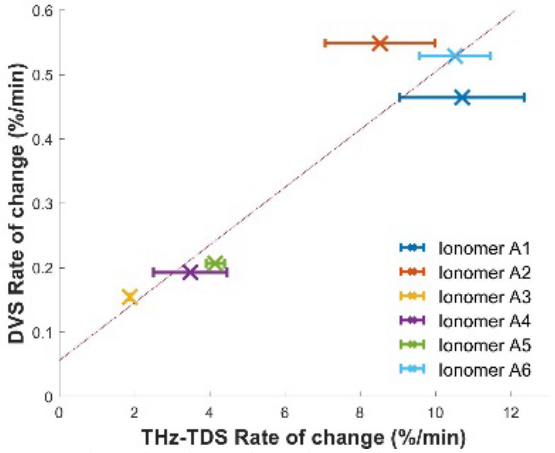

Fig. 1. Comparison of maximum desorption rate between THz-TDS and DVS

From the THz-TDS data, we extracted the water desorption rate, which is consistent with independent gravimetric-based dynamic vapour sorption (DVS) on the same membranes as shown in Figure 1. The effect of the different heat treatment parameters on water desorption is shown in figure 2, as expected heat treatments reduce the water desorption rate due to the reduced quantity of water present and increased duration further decreases water desorption.

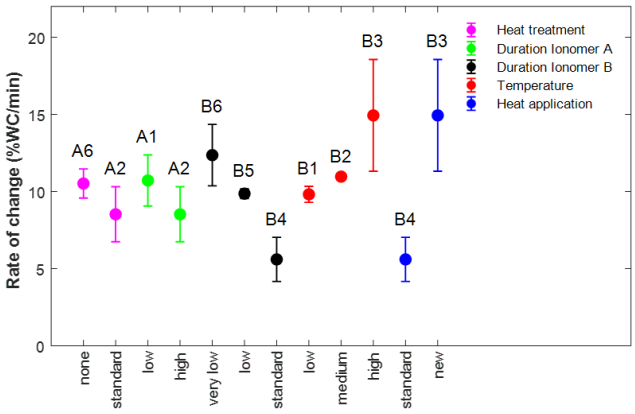

Fig. 2. Sample drying rate of membranes processed under different heat treatments

By further extracting the water states from the measurements, Figure 3 compares the effect of heat treatment, which reduces the amount of bulk water and thereby removes the crossover point, this is consistent with the reduction in proton

conductivity [8] but improves the mechanical stability of the membrane.

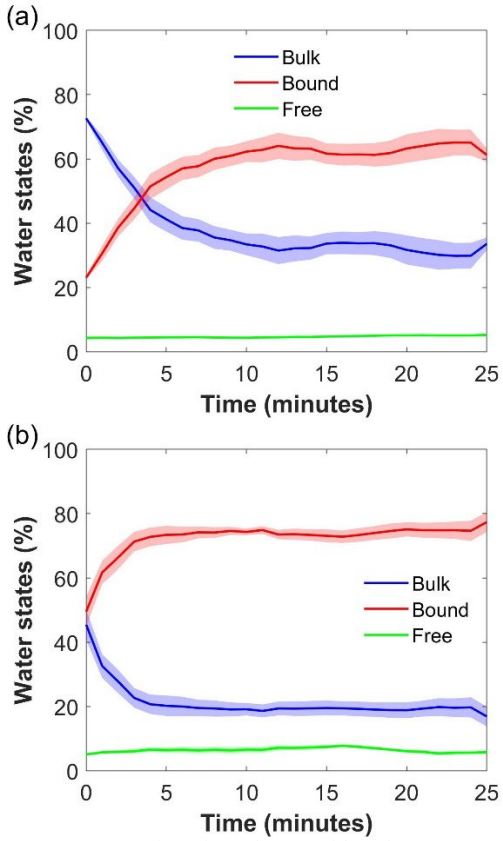

Fig. 3. Water states retention of membranes with no heat treatment (a) and heat treated (b)

Figure 4 compares bulk water contributions at t=0 with non-specific adsorbed water derived from DVS as this corresponds to water with the highest mobility and is expected to lead to increased proton conductivity [9]. A correlation is observed across all samples.

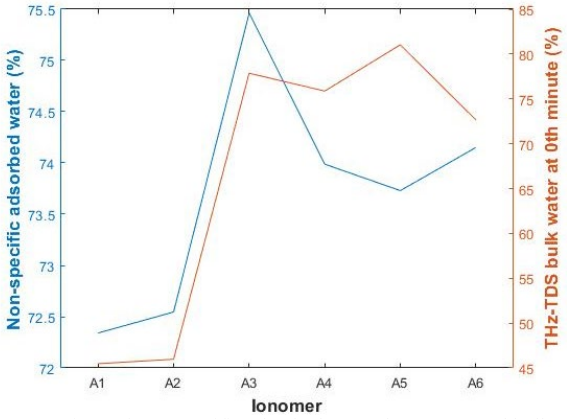

Fig. 4. Comparison of non-specific adsorbed water from DVS and bulk water from THz-TDS

As THz-TDS measurements can be acquired rapidly, we screened membranes prepared under different processing conditions as shown in figure 5 highlighting the sensitivity of the technique and the effects of heat treatment upon molecular water states caused by structural changes.

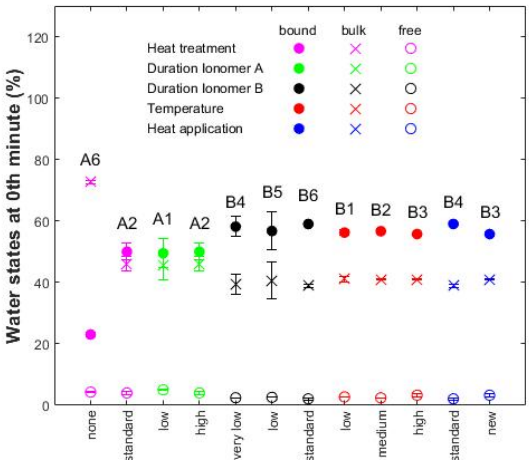

Fig. 5. Water states of membranes with different heat treatments

This work has developed a technique for quantifying molecular water states in thin films. By applying this method to membranes prepared under different heat treatment conditions we have highlighted the potential for rapid future development and optimisation of thin industrially relevant membranes [2].

ACKNOWLEDGEMENTS

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