Extracting the dielectric relaxation of water in thin Nafion membranes by terahertz spectroscopy

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***Abstract* – Terahertz time domain spectroscopy (THz-TDS) has been demonstrated to quantify water uptake and retention properties of Nafion proton exchange membranes (PEMs). With a growing interest in thinner membranes, we present the analysis technique to cater for such samples and apply it to reveal it's water uptake and retention properties.**

I. INTRODUCTION

Proton exchange membrane fuel cell has been widely applied on the energy source for electric vehicles [1] where the polymer electrolyte membrane is used for proton conduction, while simultaneously preventing electron transport and fuel cross-over. THz-TDS has previously been demonstrated to study water retention in a hydrated Nafion membrane [2] revealing the nature of water present, such as bulk, bound and free water. To date, most of the studies have been performed on relatively thick membranes eg 160 µm. At these thicknesss, existing algorithms [3], some of which are implemented in commercial parameter extraction software, can extract samples' optical constants. However difficulties arise for thin membranes eg. at 25 um where the iterative algorithm fails to converge. Here we exploit the fact that dielectric response of these hydrated membranes follows a double debye model and develop a parametric based algorithm to extract the dielectric relaxation. We validate the analysis against [4] for the same membrane thickness and apply the algorithm to extract the water retention properties of thinner membrane at 25 um.

II. METHODOLOGY

THz-TDS measurements were performed using a TERA K15 (Menlo Systems, Germany). The hydrated Nafion 117 (183 µm) and 211 (25 µm) (Fuel Cell Store, TX, USA) were measured during a 25 minutes' dehydration process at ambient conditions (T = 26°C, RH = 41%). THz waveforms were acquired at every minute interval from 5 averages. The parameteric algorithm assumes a double debye model, which is valid for these membranes [5]. To globally minimise the error function between measurement and the analytical model accounting for all etalons, a particle swarm optimisation is used. The double debye model is given by

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{[1+(i\omega\tau_1)]} + \frac{\Delta\varepsilon_2}{[1+(i\omega\tau_2)]} \quad (1)$$

where ε_∞ is infinite dielectric constant, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are defined as: $\Delta\varepsilon_1 = \varepsilon_s - \varepsilon_2$ and $\Delta\varepsilon_2 = \varepsilon_2 - \varepsilon_\infty$. ϵ_S is the static dielectric constant, ϵ_2 is the intermediate value of the real part of the dielectric constant. τ_1 is the slow relaxation time, which is regarded as 7.2 ps [5] and τ_2 is fast relaxation time.

III. RESULTS

Fig 1 shows the variation of the Debye parameters over time for both membranes. The trend of Debye parameters for two membranes is in general agreement with what is previously reported [5]. As expected, owing to a thinner membrane, Nafion 211 dries out faster than Nafion 117 thus resulting in a faster stabalisation in the double Debye parameters.

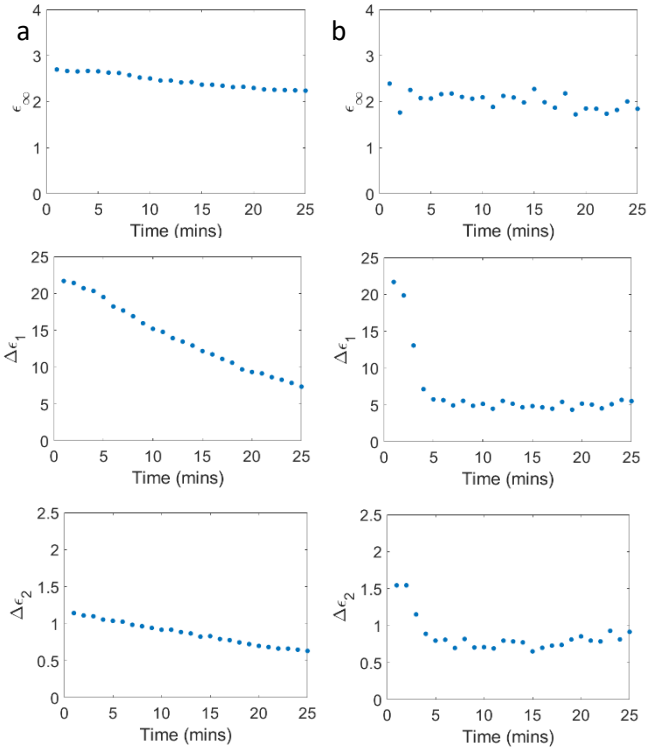

Fig. 1. The change of double Debye parameters of (a) Nafion 211 and (b) 117.

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