Water States Analysis of Anion Exchange Membranes with Terahertz Time-domain Spectroscopy

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***Abstract* –Terahertz time-domain spectroscopy (THz-TDS) has been demonstrated to resolve water states inside industrially thin fuel cell membranes. In this work, we apply THz-TDS technique to hydrated anion exchange membranes (AEMs) where detailed water information is crucial to their stability and operational performance. By performing independent ionic conductivity measurement on said membranes, we show a good correlation between the extracted conductivities and resolved bulk water of 3 different types of AEM.**

I. INTRODUCTION

Hydrogen fuel cells are at the forefront of clean energy production. Owing to the need to reduce cost especially with precious metal catalysts, there is increased attention on development and optimisation of anion exchange membrane fuel cells. Central to the operation of these fuel cells, is the water transport within the solid electrolyte membrane to facilitate charged ion movement. This water can generally be categorised as bulk, bound and free [1], depending upon the degree of hydrogen bonding. For example, bound water is generally considered as water predominately hydrogen bonded to the hydrophilic head groups in the polymer; bulk water refers to weakly hydrogen bonded water to the polymer, exhibiting co-operative reorganisation underpinning ionic conduction; free water refers to water with no-hydrogen bonding [1]. Prevailing methods of resolving water states in these membranes include nuclear magnetic resonance spectroscopy, microwave dielectric relaxation spectroscopy and differential scanning calorimetry. Compared to these techniques, THz-TDS offers a contactless testing method to rapidly screen membranes without sophisticated sample preparation and has been demonstrated to resolve the water states producing data consistent with gravimetric based dynamic vapour sorption [2]. As prior works have been only performed on proton exchange membranes [1-3], here we apply the technique to AEMs for comparison against ionic conductivity measurement.

II. RESULTS

Three HDPE-TMA based AEMs with different amination times were prepared using a pre-developed electron beam grafting method [4]. The three AEM samples are designated based on amination time, 10 minutes, 60 minutes, and 24 hours. To minimise the amount of surface water, the samples were hydrated inside a custom-made relative humidity chamber for 24 hours with deionized water. The samples were then measured using a commercial THz-TDS (K15, Menlo Systems, Germany), with the waveforms being recorded with 20 averages. The waveforms are then analysed using in-house developed code [2] to extract thickness and water states shown in Fig. 1, where the extracted thicknesses are verified by independent micrometre measurement. As can be seen, AEMs with increased grafting time resulted in ~50% bulk water at the fully hydrated state. These results indicate that the structural changes within the membrane due to increased amination time (increased number of head groups) led to more bulk water sites being formed than bound. The increase in ionic content leads to a disproportionate increase in water uptake, which at extreme levels can decrease conductivity due to the dilution of charge carrying groups. Ionic conductivity measurements on the same samples were also performed, which shows a good correlation against the THz extracted bulk water in Fig. 2. These preliminary results highlight the sensitivity of THz-TDS to examine the water states in industrially relevant AEMs, crucial to their development and optimising performance stability trade-offs.

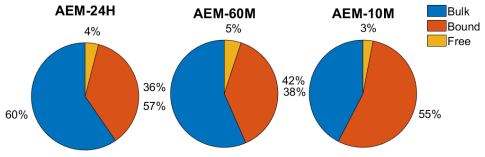

Fig. 1. Pie chart of measured water states within the AEM samples

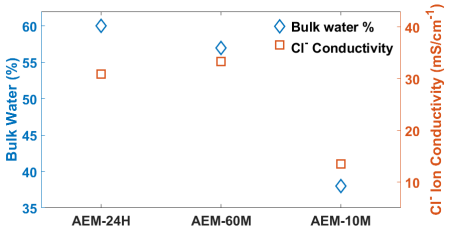

Fig. 2. Ion conductivity measurements compared to Bulk water state.

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