Does thermal treatment merely make a H$_2$O-saturated Nafion membrane lose its absorbed water at high temperature?†

Kai Feng, Lei Hou, Beibei Tang* and Peiyi Wu*

Investigating the dehydration process of a Nafion membrane helps to understand the mechanism of the decrease in its proton conductivity under high-temperature and low-humidity conditions. Herein, the influence of thermal treatment on a H$_2$O-saturated Nafion membrane was in situ studied by FTIR spectroscopy. With the aid of generalized two-dimensional correlation spectroscopy (2Dcos), the microstructural changes during the thermal treatment were discussed in detail. In short, side-chain regions first lost H$_2$O, followed by the H$_2$O loss in ionic cluster domains. It resulted in shrunk ionic channels in the Nafion membrane, which exhibited a negative influence on its proton conduction. The immediate aftermath was the crystallization of amorphous backbone regions. All these results were confirmed by TGA and XRD techniques, and the 2Dcos method was first applied in TGA and XRD results in this field.

1 Introduction

A fuel cell (FC) has long captured the attention of researchers. Nowadays, the FC has become one of the most promising technologies because it uses renewable and clean energy carriers, such as hydrogen, methane and methanol, to generate electrical power.† A proton exchange membrane fuel cell (PEMFC) outstands, especially in the application of transportation where its advantages over traditional internal combustion engines turn to be more evident.2–4 The PEMFC possesses a high energy conversion efficiency, enhanced fuel flexibility and room-temperature start-up ability. As a vital building component of the PEMFC, the PEM plays a crucial role in the PEMFC performance.5 Until now, researchers have explored various physical and chemical approaches to modify PEMs, attempting to make PEMs meet the standard for real-world applications.2,3,6,7 Meanwhile, some researchers focus on the “microstructure–property” relationship of PEMs via both experimental and theoretical methods5,8–17 from which effective guidelines for preparing high-performance PEMs are hence obtained.18,19

An ideal PEM must have high proton conductivity even under severe operation conditions. Water retention capability usually plays a decisive role in the proton conductivity of a PEM by largely affecting its ionic cluster domains.5,11,14,20,21 Good water retention capability will provide abundant H$_2$O for “proton hopping” (Grotthus mechanism) and migration of hydrated protons (H$^+$ (H$_2$O)$_n$) by which proton conduction is mainly determined.21 Nafion, for example, is one of the most investigated PEM materials. It consists of a linear polytetrafluoroethylene backbone with short, perfluroether side chains terminated by sulfonic groups. The typical phase separation leads to the formation of interpenetrating hydrophobic and hydrophilic domains in a Nafion matrix.6,7,21,24 The hydrophobic domains bestowed necessary mechanical and chemical stabilities upon the Nafion membrane, and the hydrophilic ones, often hydrated, providing well-connected ionic channels for proton conduction. However, an inevitable obstacle limits the wider application of the Nafion membrane that its proton conductivity decreases dramatically at low humidity and elevated temperature due to the fast loss of H$_2$O.

Various techniques have hitherto been employed to investigate Nafion microstructures at different hydration levels. These techniques include in situ Raman measurements,25,26 atomic force microscopy,27,28 small angle X-ray scattering (SAXS),29 small angle neutron scattering,30 neutron reflectivity,5 etc.5,11,14,16
Specially, Fourier transform infrared (FTIR) spectroscopy is a technique sensitive to the interactions between \( \text{H}_2\text{O} \) and polymers. Recently, by comparing the differences in the FTIR spectra of Nafion and its derivatives, Korzeniewski and Smotkin \textit{et al.} proposed a convincible analysis of the FTIR features of Nafion in the region from 850 to 1450 cm\(^{-1}\) \textsuperscript{1,31–33} Both of them emphasized the distinctive ability of the FTIR technique to distinguish different hydration levels of the Nafion membrane.\textsuperscript{31,33}

Additionally, Korzeniewski found that the microstructural differences in Nafion membranes produced by different preparation procedures could be also deduced by FTIR.\textsuperscript{31} Subsequently, just from an infrared-spectral insight, Hickner discovered the difference in the interactions between \( \text{H}_2\text{O} \) and fluoroalkyl-tethered sulfonated groups with different molecular structures.\textsuperscript{18}

With the aid of the attenuated total reflectance FTIR (ATR-FTIR) technique, Elabd \textit{et al.} systematically investigated the \( \text{H}_2\text{O} \) diffusion in the Nafion membrane. Accordingly, different models \textit{i.e.} diffusion–reaction and diffusion–relaxation models, determined by humidity, were hence proposed.\textsuperscript{34–37} Undoubtedly, these studies contribute to a more comprehensive understanding of the complex interplay between \( \text{H}_2\text{O} \) and Nafion.

The already-obtained knowledge has proven the intimate connection between the hydration degree and the properties of the Nafion membrane.\textsuperscript{5,31} Through comparing the FTIR spectra of wet and dry Nafion membranes,\textsuperscript{36,39} the influence of the hydration degree on its microstructures can be obtained. However, much less is known about what exactly happens in the Nafion membrane during its dehydration process. Does thermal treatment merely make a \( \text{H}_2\text{O} \)-saturated Nafion membrane lose its absorbed water at high temperature? Therefore, tracking the microstructural changes of a \( \text{H}_2\text{O} \)-saturated Nafion membrane at high temperature, especially from an \textit{in situ} point of view where some important information are probably missed by other approaches,\textsuperscript{18} will definitely give a better understanding of the proton-transport mechanisms under high-temperature and low-humidity conditions. To the best of our knowledge, no such systematic research has been conducted.

Generalized two-dimensional correlation spectroscopy (2Dcos) was first proposed by INoda.\textsuperscript{40,41} It spreads conventional spectra along a second dimension. Hence, it significantly enhances the spectral resolution by sorting the subtle features, which are hardly observable in the conventional 1D spectra. For example, with the aid of 2Dcos NMR (nuclear magnetic resonance), Schmidt-Rohr clarified the \( ^{19}\text{F} \) and \( ^{13}\text{C} \) signal assignments of Nafion. These signals were heavily overlapped in the 1D NMR spectrum.\textsuperscript{42} Meanwhile, based on the fact that different species have different sensitivities to external variables, 2Dcos can also reveal the specific sequential order of species during a certain process.\textsuperscript{41}

In this study, the microstructural changes in a \( \text{H}_2\text{O} \)-saturated Nafion membrane were \textit{in situ} tracked by the transmission FTIR technique at elevated temperature. Herein, 2Dcos analysis of FTIR helps us to understand the complicated microstructural changes greatly. What’s more, in this study, the 2Dcos method was first applied in thermo gravimetric analysis (TGA) and wide-angle X-ray diffraction (XRD) techniques in this field. And the results agreed well with those observed in 2Dcos FTIR.

Briefly, we found that side-chain regions first lost \( \text{H}_2\text{O} \). Then, the hydration level of ionic cluster domains decreased dramatically followed by the gradual crystallization of amorphous regions in the hydrophobic backbone domains. The swollen ionic channels shrunk severely during the dehydration process, negatively influencing the conduction of protons in Nafion membranes. The results obtained here may provide new guidelines for preparing high-performance PEMs under high-temperature and low-humidity conditions.

2 Experimental

2.1 Materials

Nafion solution (perfluorinated resin solution, 5 wt% of lower aliphatic alcohol and water mixture) was purchased from DuPont. The other reagents were supplied by commercial companies and used without further purification.

2.2 Preparation of Nafion membranes

The preparation method of the Nafion membrane was almost similar to that in our previous work.\textsuperscript{6,22} First, most of the solvent of the as-received Nafion solution was replaced by dimethylformamide (DMF). Subsequently, the Nafion–DMF solution was cast onto a glass mould and then the mould was horizontally placed in a vacuum oven. The temperature was slowly increased from 70 to 120 °C and maintained at 120 °C overnight. The membrane thickness was controlled around 10 \( \mu \text{m} \). After that, the membrane was immersed in 3 wt% \( \text{H}_2\text{O}_2 \) solution at 70 °C for 2 h and then boiled in 1 M \( \text{H}_2\text{SO}_4 \) solution at 80 °C for 1 h. At last, the Nafion membrane was rinsed with deionized \( \text{H}_2\text{O} \) and carefully stored.

2.3 Characterization methods

In the FTIR characterization, the Nafion membrane was immobilized in a temperature controller by being sandwiched between two pieces of ZnS crystals. The detailed information can be obtained in Fig. S1 (ESI\textsuperscript{†}): (1) bandage the border of one ZnS crystal with PTFE ribbons (Fig. S1(a, b), ESI\textsuperscript{†}), and make sure that the space between these two ZnS crystals locates on the millimetre scale, much larger than the thickness of the Nafion membrane (micrometer scale); (2) the Nafion membrane (thickness: 10 \( \mu \text{m} \)) was first saturated with \( \text{H}_2\text{O} \) by being immersed in deionized \( \text{H}_2\text{O} \) at 25 °C for 24 h. Then, it was taken out and immediately sandwiched between two pieces of filter papers to quickly remove the water on the membrane surfaces. After that, the Nafion membrane was quickly put onto the centre of the ZnS crystal evenly (Fig. S1(c), ESI\textsuperscript{†}); (3) load the other ZnS crystal onto the Nafion membrane carefully (Fig. S1(d), ESI\textsuperscript{†}); (4) pike along the PTFE ribbons to create abundant holes for \( \text{H}_2\text{O} \) desorption (Fig. S1(e), ESI\textsuperscript{†}); (5) at last, this setup (Fig. S1(e), ESI\textsuperscript{†}) was put into a temperature controller before being placed in the Nicolet Nexus 6700 FTIR spectrometer, as shown in Fig. 1. These special designs aim to dramatically weaken the influences of the “ZnS sandwiching procedure” on constraining the \( \text{H}_2\text{O} \) desorption and the macromolecular relaxation of Nafion polymer chains.
during the following thermal treatment; (6) the sample temperature was quickly elevated to the desired point (195 °C) and then maintained during the entire measurement. The FTIR spectra, with a resolution of 4 cm⁻¹ and 32 scans, were collected as soon as the sample temperature reached 195 °C in an air atmosphere. The whole equipment in Fig. 1 was swept by slow dry-air flow during the entire measurement.

All the recorded FTIR spectra were selected to conduct 2Dcos analysis. Typically, the original 1D FTIR data were carried out using a 2D software program developed by Shigeaki Morita (Kwansei Gakuin University, Nishinomiya, Japan; this 2D software is named as 2D Shige.). Then, they were further plotted into contour maps using the Origin Program. In all the contour maps, the red (warm) colours referred to positive intensities, while the blue (cool) ones represented negative intensities.

To investigate the decomposition processes of Nafion membranes by the FTIR technique, a dry Nafion membrane in H⁺-form or Na⁺-form was obtained by drying at 90 °C for 24 h. Subsequently, such a “dry” Nafion membrane was placed into a Nicolet Nexus 6700 FTIR spectrometer via the same procedures as described above. The temperature increased from 125 to 400 °C at the rate of 1 °C min⁻¹. With the aid of a macro program, the FTIR data were collected as a function of time with an acquisition time interval of 60 s.

For TGA and XRD characterization methods on the dehydration process of Nafion, 15 pieces of 1 cm × 1 cm H₂O-saturated Nafion samples were placed in a vacuum oven at 195 °C. 10 min later, one sample was taken out every other 10 min and stored carefully in a sealed bottle until all the membrane samples were collected. The atmosphere was air in the vacuum oven, and choosing “a vacuum oven” was aimed to provide a stable environment, which was almost similar to that during the FTIR measurements. The first Nafion sample for TGA and XRD characterization methods was marked as “0 min sample”. Hence, the investigated times of thermal treatment in these characterization methods were the same as that in FTIR: ~160 min. The TGA and DTG curves were obtained on the Perkin-Elmer Pyris-1 equipment in a N₂ atmosphere at the rate of 20 °C min⁻¹. XRD was performed using a PANalytical X’pert diffractometer with Cu Kα radiation. 2Dcos analyses on the TGA and XRD data were conducted through the same procedure as that on FTIR spectra.

3 Results and discussion
3.1 Analyses of conventional 1D FTIR spectra and 1D TGA curves

Fig. 2(A) presents the time-dependent 1D FTIR spectra of a H₂O-saturated Nafion membrane (thickness: 10 μm) at 195 °C. The doublet at 960 and 980 cm⁻¹ is attributed to the stretching vibrations of the –COC– linkages in the side chains of Nafion. Specifically, the former absorption mainly corresponds to –COC– closer to –SO₃H/backbone (marked as “–COC–(A)”, Fig. 2(C)), while the latter one is largely due to the –COC– in proximity to the backbone (marked as “–COC–(B)”, Fig. 2(C)). The peak at 1055 cm⁻¹ is ascribed to the symmetric stretching vibrations of the Nafion polymer: the –COC– linkage close to the –SO₃H/backbone is labelled as –COC–(A/B), respectively.
vibration of $-\text{SO}_3^-$ - Usually, $-\text{CF}_2$-groups present their symmetric and asymmetric stretching vibrations at 1151 and 1213 cm$^{-1}$, respectively.\textsuperscript{6,22,39,44} Unfortunately, these two peaks are difficult to be identified in Fig. 2 due to their over-range IR absorptions here. The membrane sample, though with a thickness of only 10 $\mu$m, is still too thick for transmittance infrared spectrophotometry.\textsuperscript{31} Indeed, making a thinner Nafion membrane facilitates the identification of $-\text{CF}_2$- groups in the FTIR spectrum. In the existing research studies on the interactions between $\text{H}_2\text{O}$ and Nafion, (spinning) coating a very small quantity of Nafion solution onto Nafion (like ZnS) is an often-used method to prepare (ultra)thin Nafion membranes (nanometres in thickness).\textsuperscript{33,45} Under this circumstance, the FTIR peaks of CF$_2$ groups could be easily identified. However, unlike bulk Nafion membrane (normally $\geq 10 \mu$m), thin Nafion films exhibit a very different physicochemical behaviour due to confinement.\textsuperscript{45-47}

The near-interface regions account for a significant volume fraction of a thin Nafion membrane, and hence its properties are not predominantly dominated by the bulk material.\textsuperscript{47} Recently, Debenedetti and his co-workers revealed that the surface structure of a thin Nafion membrane played a crucial role in its water-transportation behavior.\textsuperscript{8} Previously, our group prepared several types of high-performance Nafion-based PEMs under low-humidity and high-temperature conditions.\textsuperscript{6,7,22} Therefore, from a real-world application point of view, revealing what happens during the thermal treatment of a bulk Nafion membrane is much more meaningful. It may provide a useful guide for preparing high-performance PEMs in the future. This is the reason we choose a 10 $\mu$m Nafion membrane in this study. Of course, a thicker Nafion membrane would make it harder to identify the FTIR peaks corresponding to other functional groups. Herein, the information about the backbone changes during the thermal treatment can be obtained from the shoulder peak at 999 cm$^{-1}$ which is supposed to be corresponding to $-\text{CF}_2$- in the crystallized domain (more information is shown in Section 3.2).

As is well known, for Nafion, the proton of $-\text{SO}_3\text{H}$ prefers to dissociate from $-\text{SO}_3^-$. The electron-withdrawing nature of perfluoralkyl tether structure makes $-\text{CF}_2\text{SO}_3\text{H}$ a superacid.\textsuperscript{18,21} As $\text{H}_2\text{O}$ migrates out of the Nafion membrane, $-\text{SO}_3^-$ becomes protonated, leading to the formation of $-\text{SO}_3\text{H}$. This transition changes the local point group symmetry from $C_4$ to $C_{3v}$\textsuperscript{31,38} causing the peak intensity at 1055 cm$^{-1}$ ($-\text{SO}_3^-$) to decrease apparently during the dehydration process (Fig. 3). Moreover, this IR peak presents a slight blue-shift phenomenon. It is stemmed from the reduced hydrogen bonding interactions between $-\text{SO}_3^-$ and $\text{H}_2\text{O}$. Meanwhile, it is found that the peak intensity at 960 cm$^{-1}$ ($-\text{COC(A)}$) is also sensitive to the hydration degree of the Nafion membrane. For a hydrated Nafion membrane, $\text{H}_2\text{O}$ mainly exists in the hydrophilic (SO$_3^-$)$_n$ domains.\textsuperscript{14,16,18,39} Thereby, $-\text{COC(A)}$ is probably also embedded in a (H$_2$O)$_m$ cluster.\textsuperscript{31,32} Interestingly, the changes of peak intensities of $-\text{COC(A)}$ and $-\text{SO}_3^-$ present a good synergy, as illustrated in Fig. 3. This phenomenon indicates that the hydration degree of $-\text{COC(A)}$ extremely relies on that of $-\text{SO}_3^-$.\textsuperscript{33,48} That’s why $-\text{COC(B)}$ receives little influence from the dehydration process. $-\text{COC(B)}$ locates far away from the hydrophilic domains. As a result, the peak at 980 cm$^{-1}$ changes little during the dehydration process (Fig. 2(A)).\textsuperscript{39}

It is noteworthy that the dehydration process leads to the appearance of two new IR peaks at 915 cm$^{-1}$ and 1415 cm$^{-1}$. The former one can be attributed to the rocking vibration of $-\text{SO}_3^-$,\textsuperscript{49} while the exact assignment of the latter one is still in controversy.\textsuperscript{39,50} The unavoidable alkyl impurities in the original Nafion solution may contribute to the IR absorption here due to the bending vibrations of CH$_{1(2)}$.\textsuperscript{50} However, it cannot provide a clear physical or chemical explanation for the increasing peak-intensity phenomenon under the thermal treatment. Espuche \textit{et al.} revealed that dozens-of-days hydro-thermal aging led to the formation of sulfonic anhydride groups in the Nafion matrix.\textsuperscript{51} It resulted in the growth of a new IR peak at around 1440 cm$^{-1}$ in the aging time dependent FTIR spectra of Nafion membranes.\textsuperscript{51} However, we doubt that 3 hours of thermal treatment during the FTIR characterization has a comparable influence on the Nafion matrix.

Herein, temperature-dependent FTIR spectra of dry Nafion membranes (also 10 $\mu$m) in H$^+$-form and Na$^+$-form were collected during a heating process from 125 to 400 $^\circ$C at a rate of 1 $^\circ$C min$^{-1}$ (Fig. 4). As elucidated in Fig. 4 and 5, for the H$^+$-form Nafion, the peak intensity at 1415 cm$^{-1}$ first increases and then starts to decrease at 225 $^\circ$C. It almost disappears when the temperature reaches 400 $^\circ$C. While for the Na$^+$-form Nafion, its peak intensity changes little in the range of 125 to 400 $^\circ$C. As is well known, for Nafion, only its $-\text{SO}_3\text{H}$ group decomposes below 400 $^\circ$C. The decomposition temperatures of its side chain and backbone reach as high as 450 $^\circ$C and 500 $^\circ$C, respectively.\textsuperscript{22} So it is believed that the peak at 1415 cm$^{-1}$ is due to the functional groups in the ionic cluster domains. Therefore, we tentatively attribute it to the bending vibration of O–H in the $-\text{SO}_3\text{H}$ group. Such a kind of proton is known as the “condensed proton”. The increase in its peak intensity is a result of its increasing quantity during the dehydration process.\textsuperscript{50} Several researchers have demonstrated the presence of $-\text{SO}_3\text{H}$ in Nafion membranes under various chemical conditions by employing different techniques, such as fluorescence spectroscopy,\textsuperscript{52} SAXS,\textsuperscript{53,54} dielectric spectroscopy.\textsuperscript{54} The experimental result presented in this work provides probable FTIR evidence for the presence of $-\text{SO}_3\text{H}$ in the Nafion membrane.
As is well known, H\textsubscript{2}O is sometimes considered as a plasticizer in polymeric materials. When the H\textsubscript{2}O-saturated Nafion membrane loses most of the water in its side-chain regions and hydrophilic domains, the dehydration process is succeeded by the annealing process of the amorphous Teflon-like regions of Nafion backbones. Herein, we also collected the time-dependent transmission FTIR spectra of a dry Nafion membrane (thickness: 10 \( \mu \)m) at 195 \(^\circ\)C (Fig. S2, ESI†). It is noticed that trace amounts of H\textsubscript{2}O still remain in the hydrophilic ionic domains of this “dry” Nafion membrane. They migrate out of the membrane matrix during the successive heating steps, leading to the formation of –SO\textsubscript{3}H. Therefore, the IR peak at 1415 cm\(^{-1}\) increases obviously. However, the other IR peaks present very slight changes. This observation illustrates that removal of H\textsubscript{2}O contributes a lot to the annealing process of the amorphous Teflon-like regions of Nafion.

Second, under low-temperature conditions, Nafion probably cannot lose most of its bonded water, which cannot provide comprehensive information of its dehydration process. Sometimes, a certain amount of bonded water is stable in the Nafion matrix even when the temperature reaches up to 160 \(^\circ\)C. Besides, the Nafion membrane dehydrates very slowly at lower temperatures, which is not convenient for the FTIR and the following TGA and XRD characterization methods. As shown in Fig. S3 (ESI†), we also investigate the microstructural changes of a H\textsubscript{2}O-saturated Nafion membrane at 125 \(^\circ\)C by FTIR. Under this circumstance, the investigated time needs to be extended to at least 10 h. On average, 195 \(^\circ\)C was chosen as the investigated temperature in this study.

The findings in Fig. 2 parallel the phenomenon in the TGA characterization (Fig. 6). In fact, FTIR is an indirect technique to make affirmations about the Nafion morphology with respect to crystallization. Therefore, by the TGA technique, we explored the decomposition processes of different H\textsubscript{2}O-saturated Nafion membranes, which were pre-treated at 195 \(^\circ\)C for different minutes. Higher decomposition temperature of backbones can be found in the Nafion membrane, which is pre-treated at 195 \(^\circ\)C for a longer time, if there is indeed a crystallization process taking place in the Nafion matrix during thermal treatment. As shown in Fig. 6(D), upon extending the thermal treatment time, the decomposition temperature of its backbones increases from 511 \(^\circ\)C to nearly 528 \(^\circ\)C. Such an obviously enhanced thermal stability of Nafion backbones derives from the strengthened interactions among Nafion polymer chains. It indicates the increase in quantity and/or size of the crystallized domains in the Nafion membrane during the thermal treatment (more discussion can be found in Section 3.3).

At the same time, a similar trend can be found in the desulfonation temperature (Fig. 6(C)). It first climbs quickly to almost 373 \(^\circ\)C in about 30 min of dehydration time and then further increases to 378 \(^\circ\)C. Most of the H\textsubscript{2}O migrates out of the
hydrophilic domains at the early stage of dehydration. Hence, the dramatically strengthened interactions among –SO$_3^-$-/SO$_3$H groups enhance the thermal stability of the hydrophilic domains. Possibly, the aforesaid crystallization process in the amorphous backbone regions also contributes to the increased desulfonation temperature by better protecting the shrunken hydrophilic domains. It is worth noting that the investigated conditions for the FTIR and TGA analyses on the microstructural changes of Nafion are exactly the same: 195 °C, and in an air atmosphere. Whether the TGA and DTG curves are obtained under air or N$_2$ atmosphere has little influence on the conclusions of the effect of thermal treatment on Nafion decomposition behaviours, only if all the Nafion samples were TGA-analyzed under the same atmosphere.

3.2 2D analyses of FTIR spectra and TGA curves

2Dcos analyses can tell more about what happens inside the Nafion membrane during its dehydration process. As shown in Fig. 7(A), there are three auto peaks locating at 915, 960, and 1055 cm$^{-1}$ in the synchronous maps. It points out that the prominent changes go to –COC–(A) and –SO$_3$H groups during the dehydration process. It coincides well with the discussion concerning the 1D FTIR spectra in Section 3.1.

While with respect to the asynchronous map, it is usually adapted to improve the spectral resolution. The asynchronous map in Fig. 7(B) identifies the subtle IR peak at around 999 cm$^{-1}$ which is heavily overlapped by the bands of –COC– in the conventional 1D FTIR spectra (Fig. 2(A)) (also confirmed by the 2nd derivatives in Fig. S4, ESI$^+$). Through a very close observation in the inset of Fig. 2(A), this peak grows slightly evident when H$_2$O migrates out of the Nafion membrane. Smotkin also mentioned this peak in his recent work, although he didn’t give a clear assignment to this peak.$^{31}$ Here, considering the crystallization phenomenon in the amorphous backbone regions during the dehydration process, we attribute this peak to the stretching vibration of backbone –(CF$_2$)$_n$– in the crystallized domains. This interpretation is not in agreement with the assignment by Vito Di Noto. He ascribed it to the antisymmetric mode of –COC–(A).$^{39}$ Moreover, the band at 1055 cm$^{-1}$ splits into two bands in the asynchronous map, namely 1053 and 1060 cm$^{-1}$. As is well known, forming hydrogen bonding interactions with H$_2$O will make the stretching vibrations shift to a lower wavenumber. Therefore, the former band is assigned to –SO$_3$H$\cdots$H$_2$O, while the latter one corresponds to –SO$_3$H$\cdots$nH$_2$O ($n > m$). It is worth noting that no auto or cross peaks in the region of 1100–1300 cm$^{-1}$ were considered because of their over-range IR absorption. In other words, no convincing information could be obtained from this region.

Fig. 6  TGA curves (A), DTG curves (B), desulfonation temperature (C) and backbone-decomposition temperature (D) of H$_2$O-saturated Nafion membranes (thickness: 10 μm) which have been pre-treated at 195 °C for different minutes.

Fig. 7  2Dcos FTIR synchronous (A) and asynchronous (B) maps of the time-dependent transmission FTIR spectra of a H$_2$O-saturated Nafion membrane at 195 °C. Warm colours (red colours) refer to positive intensities, while cool colours (blue colours) refer to negative ones.
In addition to enhancing the spectra resolution, 2Dcos can also discern the specific sequential order of all the functional groups described above.\textsuperscript{40,41} The judging principle is also generalized by INoda, that is, if the cross peaks ($v_1$, $v_2$, and assume $v_1 > v_2$) in the synchronous and asynchronous maps present the same signal, the change at $v_1$ occurs earlier than or prior to that of $v_2$, and vice versa. The method for the determination of sequential order could be obtained from our previous work.\textsuperscript{43} Briefly, multiplication is performed on two signs of each cross peak in both the synchronous and asynchronous maps.\textsuperscript{43} The detailed spectral reading procedures are not provided here, and the final results are presented in Table 1. Based on Noda’s rule, the sign labelled as “+” refers to the top wavenumber corresponding to the external perturbation earlier than the left one. If the left wavenumber corresponds to earlier than the top one, the sign is marked by “−”. Therefore, the overall sequential order during the dehydration process is deduced as follows (“→” means prior to or earlier than): 915 cm\textsuperscript{−1} → 1053 cm\textsuperscript{−1} → 960 cm\textsuperscript{−1} → 1060 cm\textsuperscript{−1} → 999 cm\textsuperscript{−1}.

Table 1 The final results of multiplication on the signs of each cross peak in the 2Dcos FTIR synchronous and asynchronous maps of a H\textsubscript{2}O-saturated Nafion membrane at 195 °C

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Fig. 8 (A) Schematic illustration of the dehydration process of a H\textsubscript{2}O-saturated Nafion membrane at elevated temperature; and (B) schematic indication of the shrunken ionic channels due to the H\textsubscript{2}O loss and the increase in the quantity and/or size of crystal domains in the Nafion membrane.
This description is not firmly demonstrated by the experimental results in this study and needs more evidence.

The 2Dcos technique has universal applicability and can be used in any form of analytical techniques, including Raman, TGA, UV-vis, NMR, XRD, fluorescence, etc.\textsuperscript{55, 56} Fig. 9 presents the 2Dcos TGA synchronous and asynchronous maps of a H\textsubscript{2}O-saturated Nafion membrane at 195 °C. The decomposition temperatures at 362 and 522 °C have a positive cross peak in the 2D TGA synchronous map (Fig. 9(A)). It indicates that the thermal stabilities of ionic domains and backbone regions have the same response to the dehydration process at 195 °C. That is, both of them are enhanced, as demonstrated by the raw TGA curves in Fig. 6. Meanwhile, thanks to the distinctive capability of asynchronous spectra (Fig. 9(B)), the peak corresponding to the decomposition process of Nafion side chains is detected here (470 °C). And the sequential order is deduced as follows: 470 °C (side chains) \rightarrow 362 °C (–SO\textsubscript{3}H groups) \rightarrow 522 °C (backbones). In other words, the side-chain regions of the Nafion membrane dehydrate first at 195 °C, followed by the hydrophilic ionic domains. Subsequently, amorphous hydrophobic backbones crystallize. This is another reason that we ascribe the IR peaks at 915 and 999 cm\textsuperscript{-1}, respectively to the rocking vibration of –COC–(A) and the stretching vibration of backbone –(CF\textsubscript{2})\textsubscript{n}– in the crystallized domains. The results in 2Dcos TGA are in good agreement with those found in the 2Dcos analysis of FTIR. It renders the reliability of the proposed mechanism describing the influence of thermal treatment on microstructures of a H\textsubscript{2}O-saturated Nafion membrane (Fig. 8(A)).

3.3 1D/2D analyses of XRD curves

The XRD technique has distinctive advantages to investigate the microstructures of Nafion. We also characterized the H\textsubscript{2}O-saturated Nafion membranes (thickness: 10 μm), pre-treated at...
195 °C for different minutes via the same procedures as those in TGA, by the XRD technique, trying to provide more firm evidence for the detailed conclusions drawn in Section 3.1–3.2. Generally, a doublet is often observed at around 2θ = 17° in the XRD pattern of Nafion. The relatively broad peak at 2θ = 16.1° is attributed to amorphous regions of Nafion, while the narrow one at 2θ = 17.7° is due to its crystalline regions. As shown in Fig. 10(A), its peak intensity decreases gradually during the dehydration process. It can be explained by the weakened difference in the electron densities between the hydrophobic and hydrophilic regions which is stemmed from the dramatic loss of H2O in ionic clusters (Fig. S6, ESI†). Meanwhile, the value of Acry/(Acry + Amo) increases upon extending the dehydration time (Fig. 10(B)). Acry/(Amo) refers to the integral area of the decomposed peak corresponding to crystalline (amorphous) regions, and the detailed information of peak splitting can be obtained from Fig. S5 (ESI†). It seems that all the crystallizable TFE units of Nafion, below 70% of its total TFE units, crystallize at ≥120 min of dehydration times (Fig. 10(B)). Generally speaking, the FWHM of the peak corresponding to the crystalline regions increases slightly during the entire dehydration process, while that of the amorphous regions decreases (Fig. 10(C and D)). Hence, except for the increase in domain size of the existing crystalline regions, the crystallization process may also result in the formation of more crystalline domains with different sizes in the Nafion matrix.33

Considering that XRD can reveal the changes in both crystalline and amorphous regions of Nafion during its thermal treatment process, we also analyzed the XRD data (Fig. 10(A)) by the 2Dcos technique, as shown in Fig. 11. According to Noda’s rule, the sequential order is deduced as follows: 16.1° → 17.7°. That is, prior to the crystallization process, the amorphous regions first lost H2O. It is in good agreement with that obtained from 2D FTIR (Fig. 7) and 2D TGA (Fig. 9).

4 Conclusions

Herein, the microstructural changes of a H2O-saturated Nafion membrane under high-temperature conditions is investigated in detail by the transmission FTIR technique and the 2Dcos method. Briefly, for a H2O-saturated Nafion membrane, the part of its side chains in proximity to –SO3− is also embedded in an aqueous phase. It first dehydrates during the dehydration process, followed by a dramatic loss of H2O in the hydrophilic ionic domains. Then, the amorphous backbone regions of Nafion begin to crystallize, resulting in an increase in the quantity and size of crystal domains in the Nafion membrane. Besides, systematic TGA and XRD characterization methods also provide some evidence for the proposed mechanism about the influence of thermal treatment on microstructures of a H2O-saturated Nafion membrane. The approach employed here can be facilely applied in the investigations of the dehydration process of other PEMs.

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Notes and references
