

TRA105 Fuel cell systems

Vibrational spectroscopy to study a traditional polymer electrolyte

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Fuel Cell basics

Fuel cells are one of the promising technologies in the future energy system. Due to its possibility to use a range of different fuels and virtually emission free usage it has been proposed as one of the key components in decarbonizing society. The work horse of a fuel cell is the Membrane Electrode Assembly (MEA) which is comprised of the gas diffusion layers, the catalysts layers and the membrane. In a proton exchange membrane fuel cell (PEMFC) the membrane is responsible for the conduction of protons from the anode to the cathode for the reaction of hydrogen and oxygen into water.

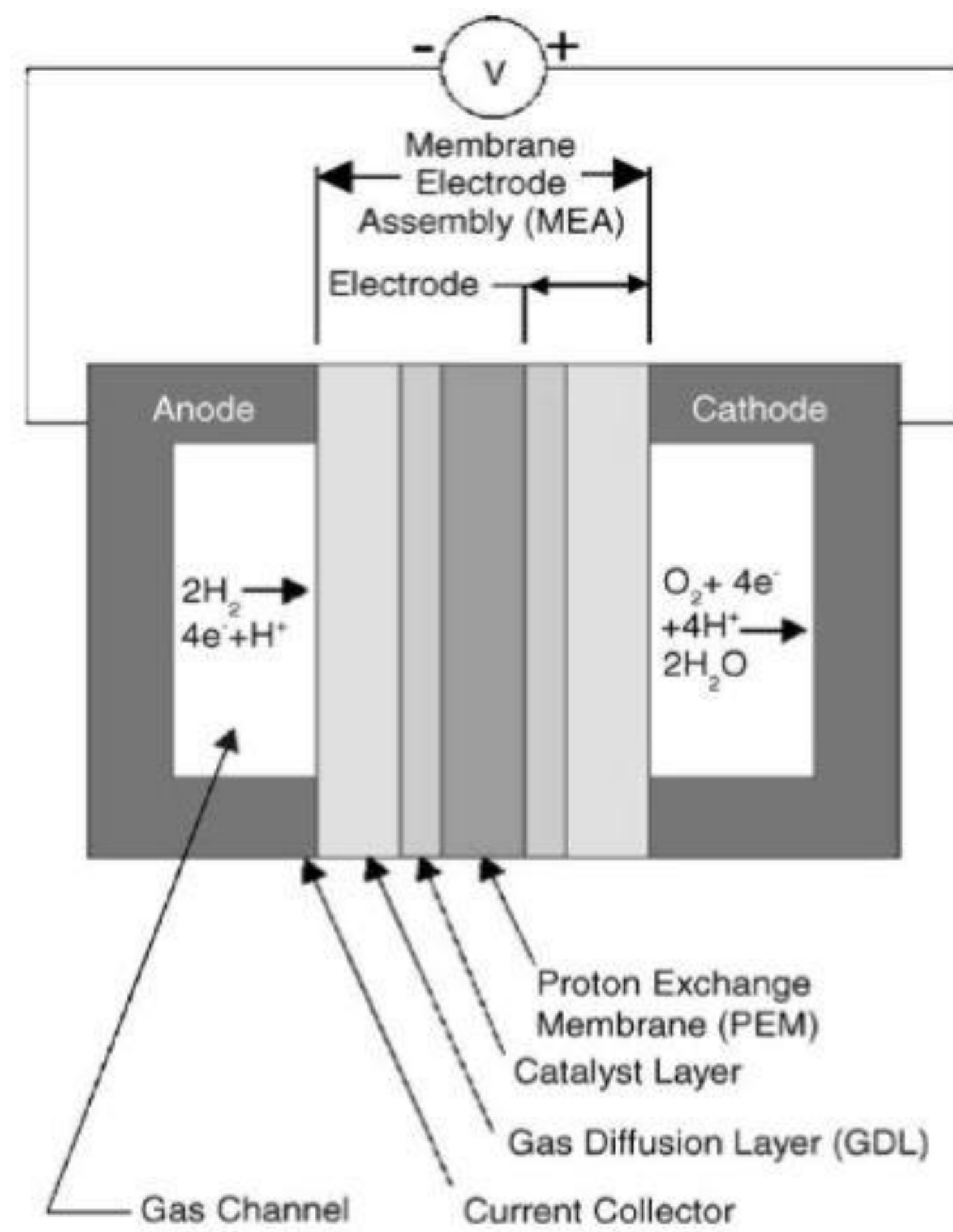


Figure 1, Fuel cell component sketch [1]

Raman spectroscopy

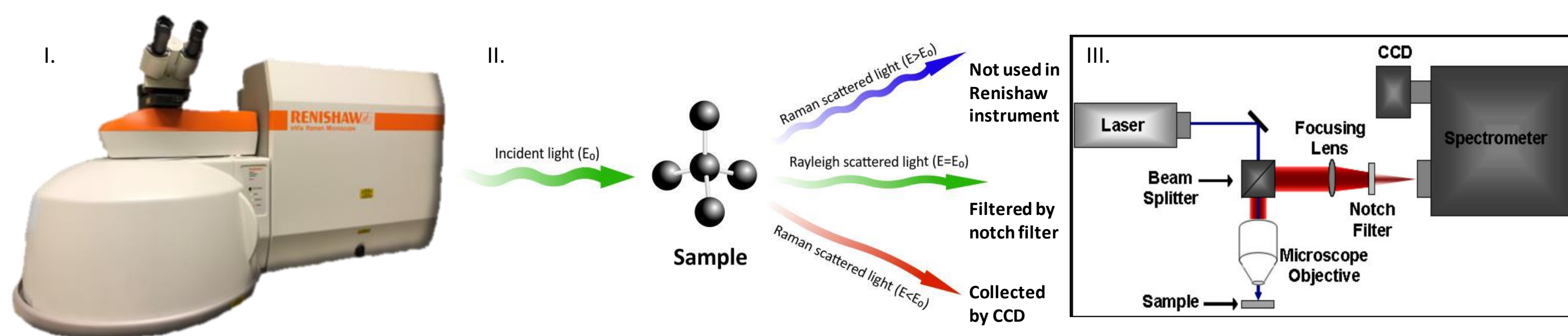


Figure 4: I. Photo of Renishaw Raman spectrometer (Photo: Hannes Kannisto). II. Raman spectroscopy principle [2]. The sample is irradiated by a laser in the visible to near infrared spectrum. The elastic scattered light (Rayleigh scattered) is filtered out by a notch filter. The inelastic scattered light is enhanced and detected by a CCD (Charge Coupled Device), that converts incoming photons to electric signals. A software processes the signals and present a Raman shift spectrum. III. Principal schematics of Raman instrumentation [3].

Methodology

Nafion® 212 membrane

Measurements were performed on the untreated Nafion® sample, with a laser at $\lambda=785$ nm. The anti-Stokes peaks between $80\text{--}2000\text{ cm}^{-1}$ were measured to detect C-F and C-S bonds in the Nafion® molecular structure. This laser was unfortunately not aligned properly causing a low signal. More severely, the Nafion® sample gave a high luminescence, leading to very low quality of the measurements. As there was no time available to adjust the alignment, some results were achieved by accumulation (repeated measurements). The results are presented in Figure 5.

Part of the Nafion® sample was then soaked in distilled water for ca 1 hour. To avoid dehydration, the sample was then put in a petri dish with distilled water and placed in the Raman microscope. Measurements were performed both on the Nafion® sample and on the water surface itself, with a laser at $\lambda=532$ nm. In this case, the alignment of the laser was not an issue. Measurements on water (between $2000\text{--}4000\text{ cm}^{-1}$ to see the O-H hydrogen bonds) resulted in a classic "double-peak" shape (not shown). On the Nafion® however, background noise due to e.g. luminescence was very high. This resulted in poor quality of the results (not presented). The sample was therefore removed from the petri dish and put on a glass plate, a small part hanging over the edge. Measurements were performed both on the main surface, inside the sample and on the cross section of the edge (Figure 6). Unfortunately, the noise from the background was still very high, impacting the results. Hence, no conclusions could be drawn from the obtained results, while these were disregarded in this study.

Nafion® D-521 dispersion

A drop of Nafion® D-521 dispersion (5 wt-% in water and 1-propanol; Alfa Aesar) was placed on a glass surface in the instrument. Measurements were made with $\lambda=532$ nm and clear peaks were obtained. The results are presented in Figure 5.

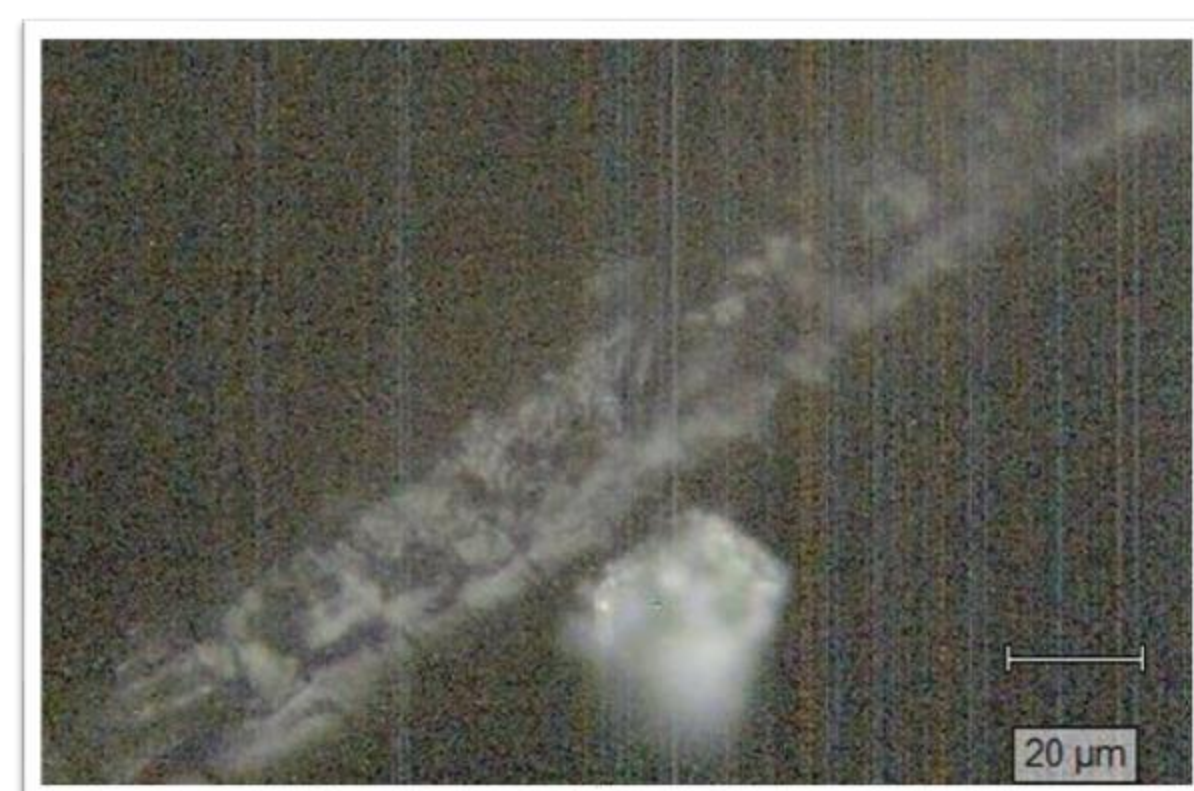


Figure 6, In situ photo of Nafion® membrane with grain reference. Taken with Renishaw Raman spectrometer.

Nafion®

Nafion® is a commercial name for the most common variant of a sulfonated polytetrafluoroethylene (PTFE) based co polymer. Invented in the late 60:s by DuPont many different alternatives of Nafion® as well as similar products have come to be invented. Nafion® products are classified according to their equivalent weight EW and thickness in thousands of inches (e.g. Nafion® 117 – 1100 EW and 0.007 "). The chemical structure of a generic Nafion® molecule can be seen below (Figure 3). Note that the lengths of chains marked x, y and z can vary. [4]

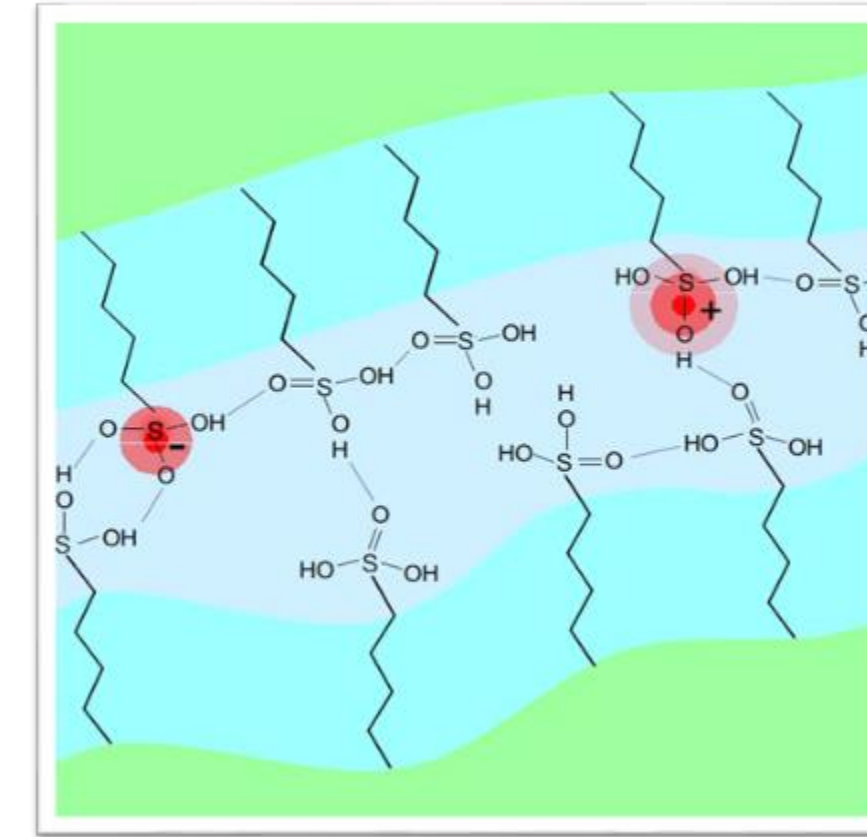


Figure 2, Illustration of microstructure of Nafion® membranes [5]

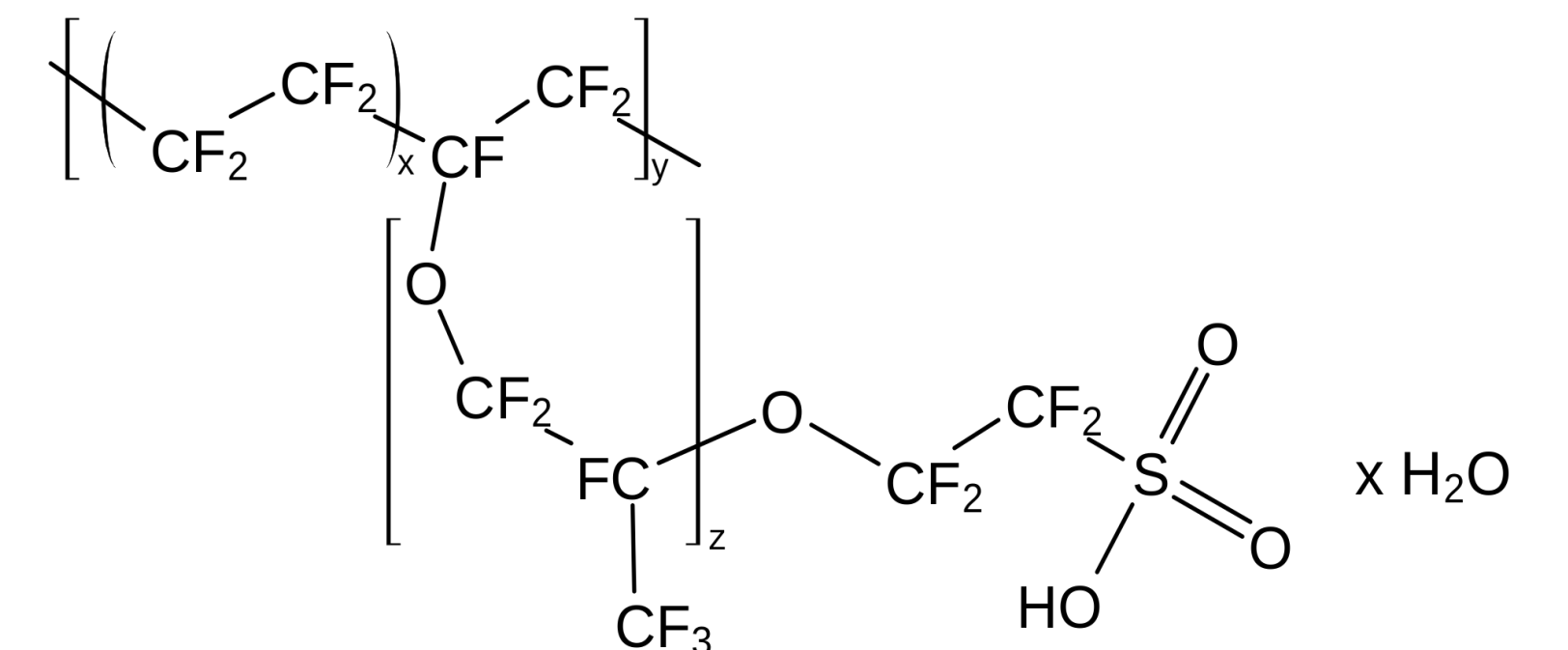


Figure 3, Chemical structure of Nafion® [6]

H⁺ conductivity in sulfonated PTFE

The excellent H⁺ conducting ability of sulfonated PTFE polymers can be attributed entirely to the sulfonic end group (R-SO₃H). The sulfonic end groups are highly hydrophilic as opposed to the PTFE which shows a strong hydrophobic behavior. This makes the material separate in regions which only have a structural importance (green in Figure 2) and regions which have a high water uptake where protons are conducted. The channel morphology is debated [7] in the literature, though there seems to be consensus regarding the channel size being in the 50 Å range. The proton conducting mechanisms of the hydrophilic region are vehicular transport, where solvated H⁺ are transported surrounded by water molecules; and the Grotthuss mechanism where H⁺ ions jump from molecule to molecule. As water is the mediator for the transport of H⁺ in all the transport cases, the ionic conductivity is highly dependent of the Relative Hydration (RH) of the membrane material. Therefore Nafion® membranes require a careful balancing in order to ensure good performance. This is often done using a humidifier on the input air stream to combat membrane drying.

Results and Discussion

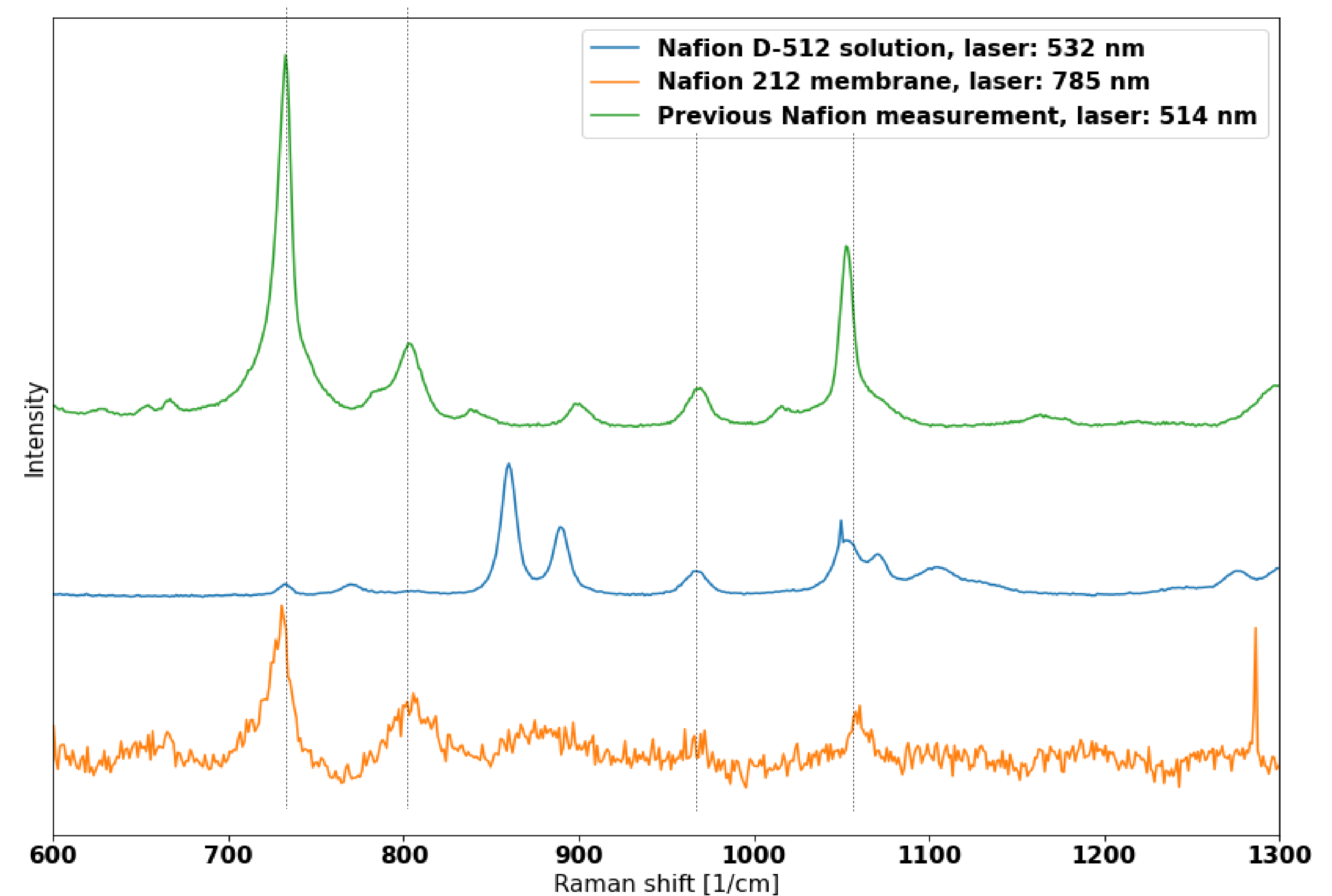


Figure 5, Raman shift of different samples. Dashed lines according to reference attributions stated in Table 1.

The spectrum of the untreated Nafion® 212 membrane (showed in Figure 5) is quite blurry due to the luminescence of the sample. Even so, some peaks can be attributed to Nafion® [8] according to Table 1. The corresponding peaks are clearly visible in the reference measurement (Nafion® Grenoble, $\lambda=514$ nm), provided by Dr Anna Martinelli, showing that the sample is indeed Nafion®. The upper spectrum, showing the Raman shift of the Nafion® D-521 dispersion, is clearly different from the other spectra, as peaks attributed to 1-propanol [9] are clearly visible. Peaks corresponding to Nafion® are also visible, although especially the peak at 1060 cm^{-1} overlap with peaks attributed to 1-propanol [8,9].

Table 1: Attribution of Nafion® peaks [5].

Attribution	Raman shift (cm^{-1})
CF ₂ symmetric stretch	~730
CS stretch	~800
COC symmetric stretch	~970
SO ₃ ⁻ symmetric stretch	~1060

Conclusions

The results show that we can identify Nafion® with Raman spectroscopy. It is clear that Raman spectroscopy can be a powerful tool to distinguish different bonds in the Nafion® structure. This can be used to determine how the water and protons interact with the membrane on a chemical level. It is also clear that getting the prerequisites right for clear results is not always easy. Instrument settings can be sensitive and sample preparation is important. The obtained results show that Nafion® can be identified. However, to get an indication of interaction between Nafion® and water and protons, more time than was available is needed.



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- References:
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