

Degradation mechanisms of PEMs investigated by

Raman spectroscopy

TRACK COURSE: TRA275 Fuel Cell Systems

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INTRODUCTION

The fuel cell industry is experiencing rapid growth as clean energy technologies advance. To improve the longevity and efficiency of fuel cells, it is crucial to investigate the degradation of proton exchange membranes. This project aims to try examining the degradation of perfluorosulfonic acid (PFSA) membranes by comparing the chemical properties of a freshly manufactured sample with those of a used membrane, using Raman spectroscopy. This analysis will provide critical insights into the degradation mechanisms and help enhance the performance and durability of fuel cells.

PFSA, or perfluorosulfonic acid, is renowned for its robust chemical and thermal stability as a polymeric membrane, boasting amphiphilic properties. However, over time, this membrane can experience various degradation mechanisms, including mechanical, chemical, and thermal factors. Chemical degradation, in particular, can initiate processes such as side chain scission and main chain unzipping. Raman spectroscopy emerges as a valuable technique in this context, facilitating the precise analysis of chemical composition and molecular structure. By plotting intensity against wavenumber (or Raman shift), Raman spectroscopy can in principle provide accurate insights into the type of degradation that has affected a PFSA membrane.

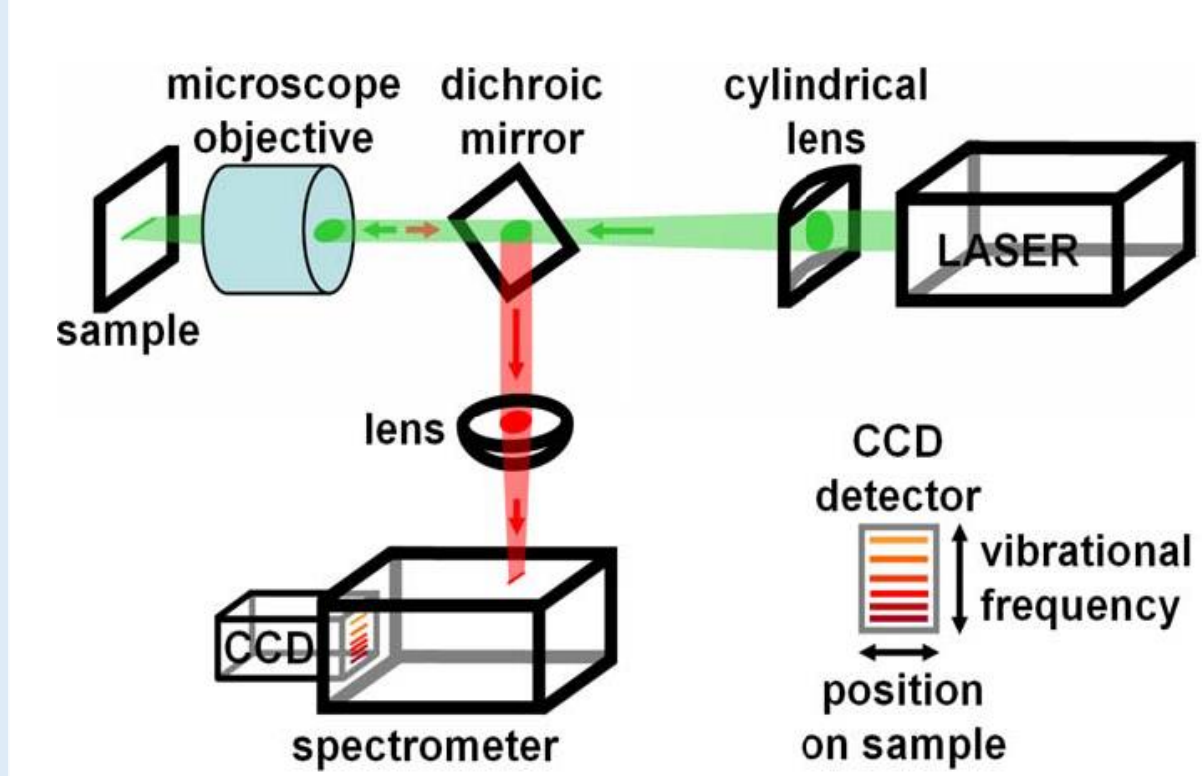


Fig 2. Raman spectroscopy [3]

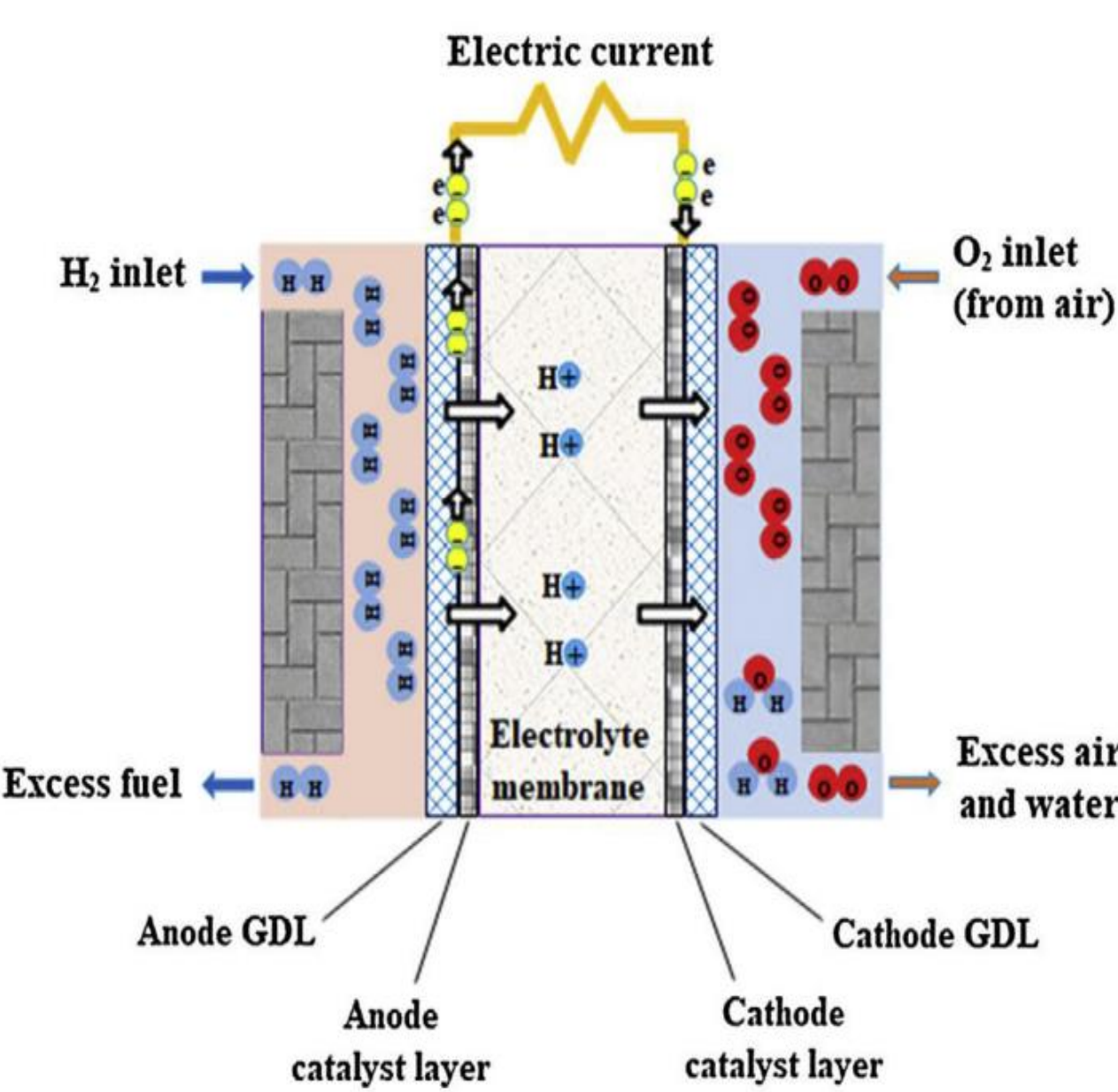


Fig 1. Operation of a PEMFC [5]

EXPERIMENT

In Raman spectroscopy, monochromatic light, typically a laser, is directed onto the sample, and the scattered light is then analyzed. The energy difference between the incident light and the scattered light relates to the energy of vibrational modes of the sample. In our experiment, we used Raman spectroscopy to examine two samples: a fresh membrane electrode assembly (MEA) and an equivalent MEA used in a fuel cell during 15,000 cycles at 120 degrees Celsius. By comparing the Raman spectra of these two specimens, we can glean insights into structural or compositional changes that occurred during the fuel cell's operational time.

In this technique, various monochromatic lights can be utilized, each with variable intensity. For this experiment, a red laser light with a wavelength of 785 nm was chosen. Calibration commenced with the use of a silicon wafer as the initial sample, referencing its first order vibration at 520.6 cm⁻¹. The carbon layer of the unused MEA was also analyzed, yielding results consistent with the expected presence of amorphous, graphitic carbon. Subsequently, the composition of the proton exchange membrane (PEM) portion of the unused MEA was established as a reference. The composition analysis of the MEA exposed to 120 degrees Celsius was then conducted across three distinct areas: the gasket layer, the MEA itself, and the intersection point between the gasket and the MEA (referred to as the corner point), alongside a defect point within the MEA. Additional measurements were taken from the gasket to distinguish its composition from that of the MEA at the intersection point. The objective is to compare the composition of the unused PEM as a reference to that of the corner and defect areas.

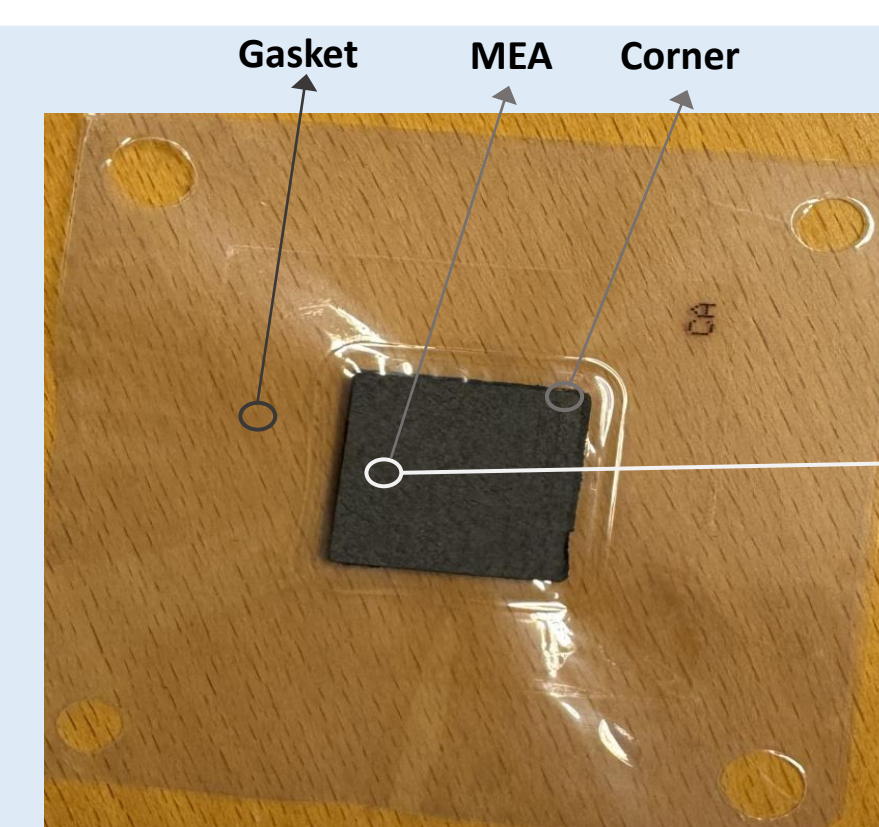


Fig 3. MEA sample

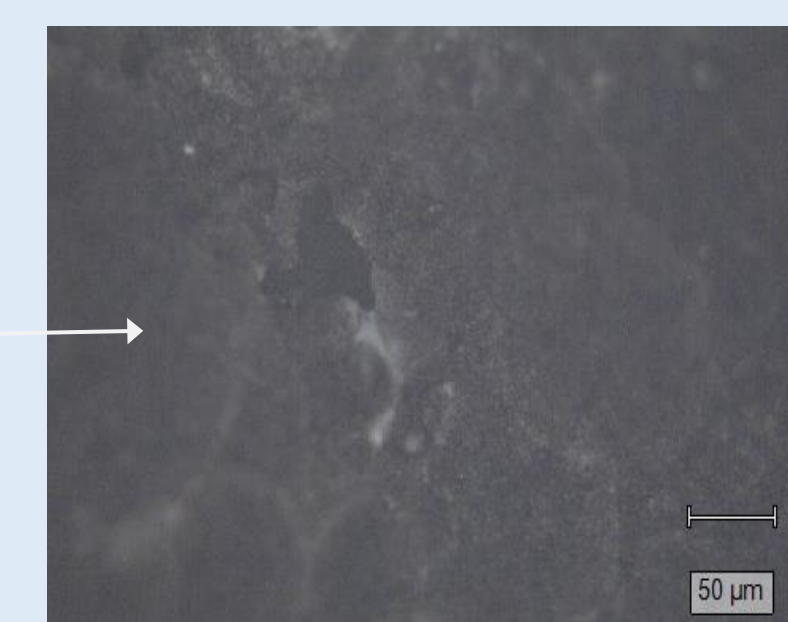


Fig 4. Defect point of the sample

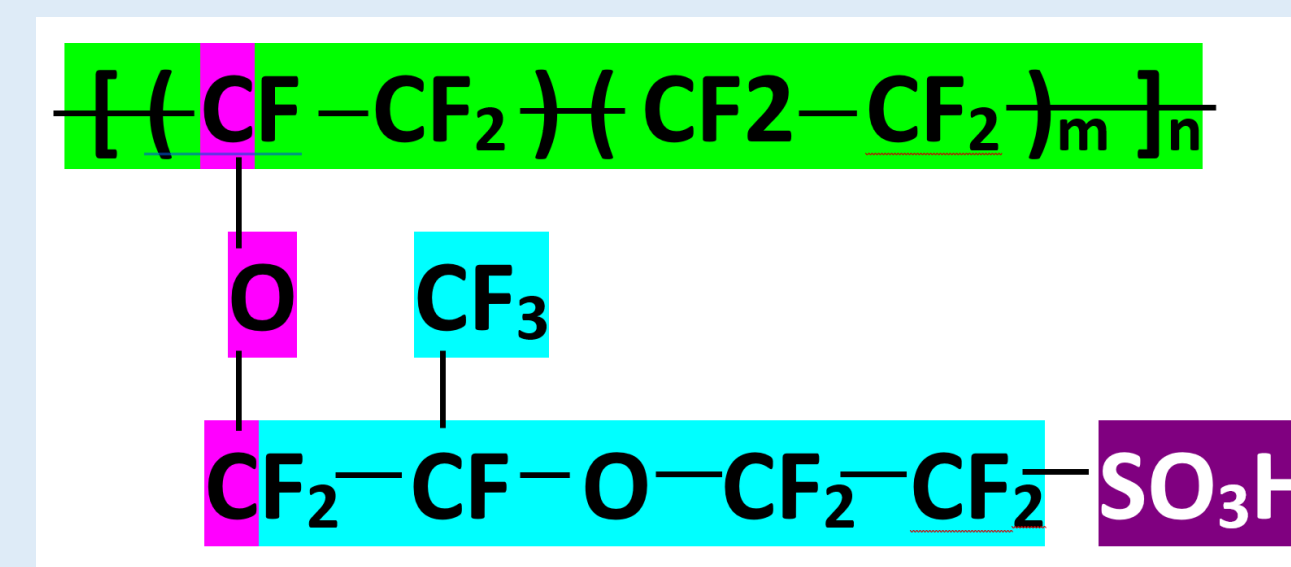


Fig 5. Chemical structure of PFSA

RESULTS

From the reference spectrum of a sample similar to the PFSA at focus in this project, peaks are observed around 732, 808, 975, and 1060 cm⁻¹ corresponding to specific chemical bonds within PFSA, as follows:

- The peak at approximately 732 cm⁻¹ is assigned to C-F bonds in the backbone structure (highlighted in green in Fig. 6)
- The peak at around 808 cm⁻¹ is assigned to C-F bonds in the sidechain (highlighted in blue in Fig. 6)
- The peak at approximately 975 cm⁻¹ is assigned to C-O-C bonds (highlighted in pink in Fig. 6)
- The peak observed near 1060 cm⁻¹ confirms the presence of S-O bonds (highlighted in purple in Fig. 6) at the end of the side chain

These findings align with the expected chemical composition of PFSA membranes, validating the utility of Raman spectroscopy for characterizing their chemical structural properties.

Raman spectroscopy was employed to examine the chemical structural properties of PFSA membranes, with the resulting data depicted in Fig. 7. A comparison was made between two MEA samples: one that was unused and another that had been subjected to 15,000 hours of use at 120 °C. The used MEA underwent analysis at multiple points to ensure robust findings (also we could find some defect spots where to measure on PFSA without disassembling (Fig. 4). In the used MEA sample, particular attention was paid to analyze the defect spots where degradation may have occurred. The resulting graph (Fig. 7) revealed a peak shift of the peak at 732 cm⁻¹, that caught our attention. It is noteworthy that similar peak shifts have been observed in some previous works. However, comprehensive research on this matter is still in progress and further investigation is required to fully understand its implications. Although the anticipated outcomes, as indicated by the reference PFSA graph (Fig. 6) with a similar chemical structure, were not obtained, a notable observation was the shift in peak intensity within the 700 cm⁻¹ to 750 cm⁻¹ range. Unfortunately, due to time constraints, further investigation into this shift was not feasible. Nonetheless, this observation presents an intriguing avenue for future research, suggesting potential changes in the chemical composition or structural integrity of the membrane upon prolonged use at high temperature.

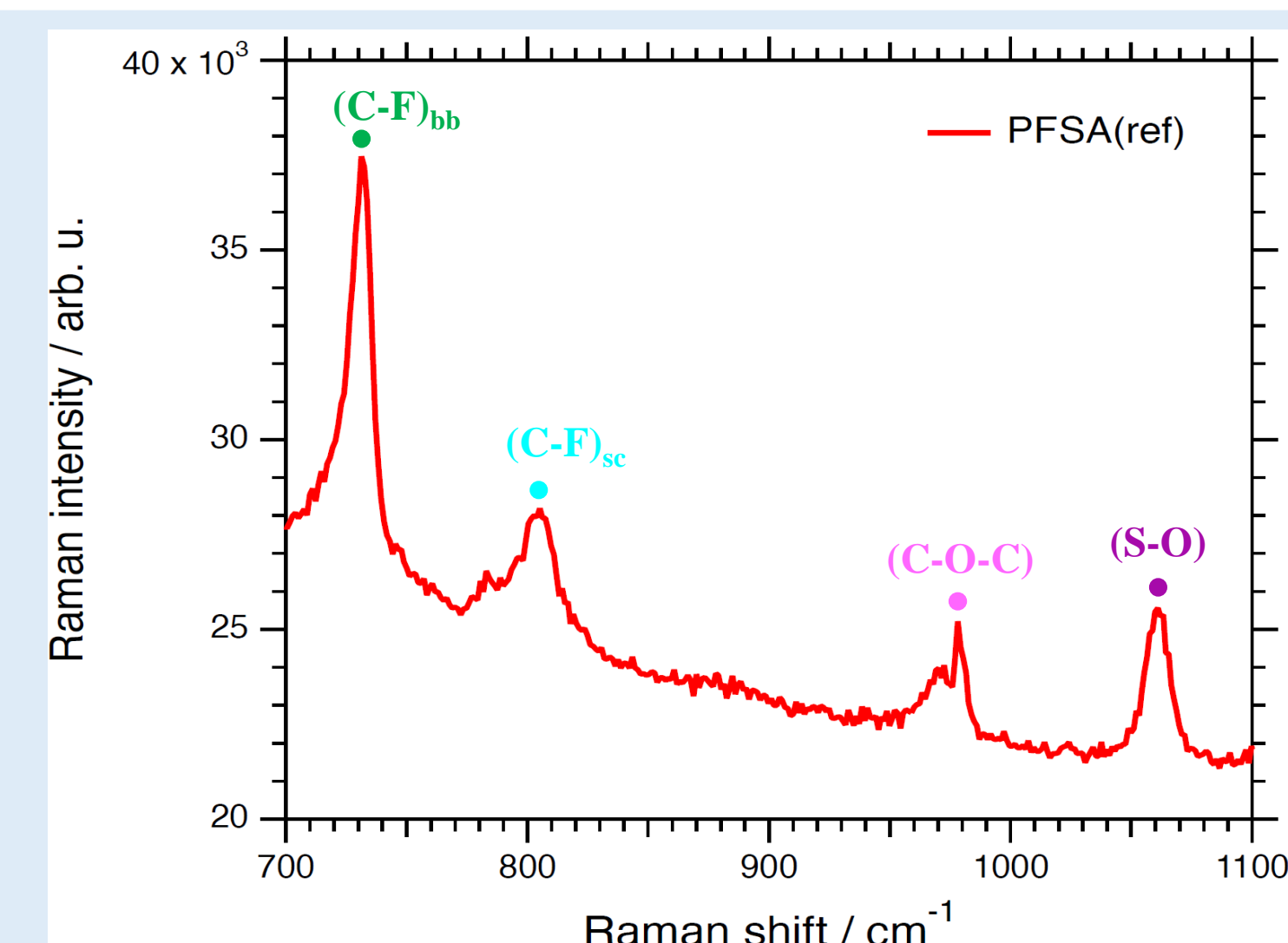


Figure 6. Reference PFSA

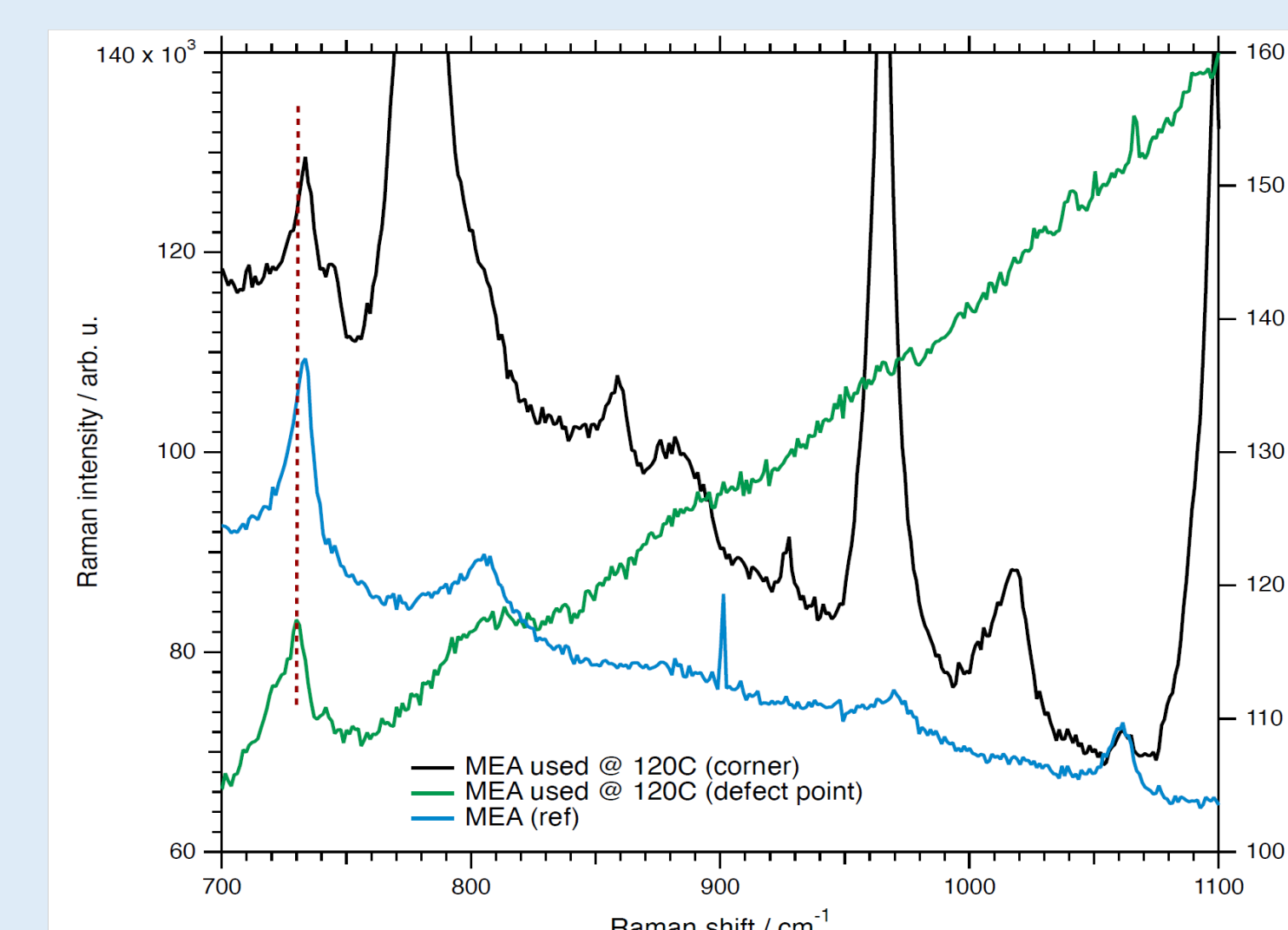


Figure 7. Final Result

DISCUSSION & CONCLUSIONS

In this study, we explored the potential of confocal Raman microscopy for analyzing ionomers employed as proton exchange membranes in fuel cells. Precise measurement settings are essential, and a calibration curve specific to the device must be established to accurately collect Raman spectra.

One intriguing observation worth further investigation is the peak shift observed around 729 cm⁻¹ in the defective region of the membrane. This shift is notable as it deviates from the peak observed at approximately 733 cm⁻¹ in the reference area and at the corner of the same membrane. Further analysis of this peak shift could provide valuable insights into the structural changes occurring within the defective portion of the membrane.

To conclude, confocal Raman microscopy shows significant potential for quantitative ionomer characterization. It serves as a valuable tool for assessing the quality of pristine membranes and as a means for quantitative analysis, providing three-dimensional insights into degraded membranes.

WAY FORWARD

Due to constraints on time and resources, the analysis couldn't be thoroughly completed. However, it is imperative to revisit and delve deeper into it, especially considering the small but significant shift observed in the spectrum. This shift requires further scrutiny and analysis to understand its implications fully.

We need to analyze the integrated area under different peaks, which were not well resolved in this project, to make quantitative conclusions.

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