



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.journals.elsevier.com/spectrochimica-acta-part-a-molecular-and-biomolecular-spectroscopy

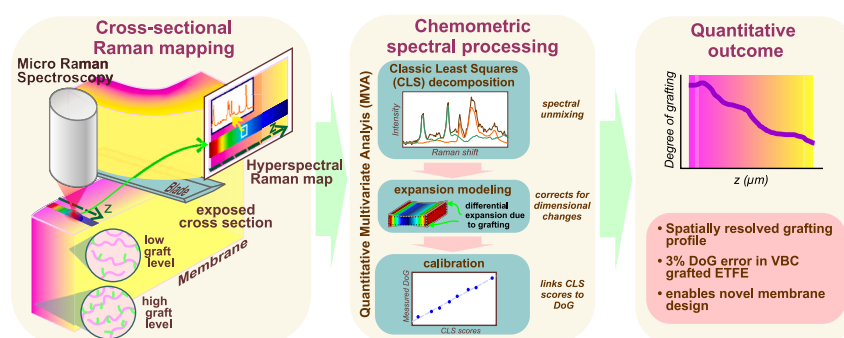
Novel chemometric Raman approach for spatially resolved quantification of graft distribution in anion exchange membranes

Allan Berezcki^{a,*}, Andrey da Silva Barbosa^a, Niklaus Ursus Wetter^a, Dario R. Dekel^b, Elisabete Inacio Santiago^{a,*}^a Nuclear and Energy Research Institute (IPEN), Av. Prof. Lineu Prestes, 2242, São Paulo 05508-000, Brazil^b Department of Chemical Engineering, Technion – Israel Institute of Technology, 3200003 Haifa, Israel

HIGHLIGHTS

- First spatial quantification of graft distribution in membranes via Raman-based multivariate analysis.
- Provides rapid, spatially resolved degree of grafting mapping with widely available tools.
- Enables design and validation of novel asymmetric membranes through local graft quantification.
- Method validated with overall degree of grafting, showing 3% deviation from calibration.
- Model accounts for membrane expansion during graft to link local and global degree of grafting.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Anion-exchange membranes
 Fuel cells
 Raman spectroscopy
 Multivariate analysis (MVA)
 Classical least squares (CLS)
 Chemometrics
 Functional copolymers

ABSTRACT

Precise control of the graft distribution, represented by the degree of grafting (DoG), in anion exchange membranes (AEMs) prepared by radiation-induced grafting (RIG), is critical for alkaline fuel cells' performance, especially aiming to improve water management. However, current methods offer only bulk or qualitative assessments of DoG, limiting the ability to understand and optimize local membrane properties. In this work, we present a novel Raman-based chemometric method for the spatially resolved quantification of DoG using micro-Raman spectroscopy. By applying classical least squares (CLS) fitting to decompose Raman spectra into contributions from the polymer base and grafted side chains, we establish a direct correlation between CLS scores and the local DoG. This approach enables, for the first time to our knowledge, the use of a multivariate technique for quantitative mapping of grafting profiles across the membrane cross-section using a widely accessible and non-destructive technique. The method is validated on membranes with known grafting levels and applied to asymmetric DoG AEMs, revealing detailed insights into spatial variations in functionalization. Moreover, the approach is broadly applicable to any grafted copolymer system with side-chain functionalization, beyond the specific membranes studied here. By combining spatially resolved measurement with rigorous chemometric analysis, this technique offers a robust tool for the design and optimization of next-generation ion-conducting membranes in electrochemical energy systems.

* Corresponding authors.

E-mail addresses: berezcki@alumni.usp.br (A. Berezcki), elisabete.santiago@usp.br (E.I. Santiago).<https://doi.org/10.1016/j.saa.2026.127558>

Received 30 October 2025; Received in revised form 15 January 2026; Accepted 4 February 2026

Available online 10 February 2026

1386-1425/© 2026 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Anion exchange membranes (AEMs) have gained increasing attention as a key component in electrochemical devices, such as AEM fuel cells (AEMFCs) [1], AEM water electrolyzers (AEMWEs) [2], and AEM oxygen separation (AEMOS) [3] thanks to their ability to operate under alkaline conditions. Operating in alkaline medium enables the use of non-noble metal catalysts, drastically reducing material costs and expanding the viability of sustainable energy conversion technologies. Despite these advantages, AEMFCs still face a critical challenge: water management. Maintaining the delicate balance between membrane hydration, drying, and flooding remains a major obstacle to long-term performance and stability [4–10].

In this context, our research group has been investigating a new class of asymmetric AEMs via radiation-induced grafting (RIG) copolymerization. RIG consists in altering the polymer matrix by incorporating polar or non-polar monomers that form covalent bonds with the polymer backbone, thereby influencing its physicochemical characteristics [11]. Such features are designed to address water management issues by tailoring the AEM structure across its cross-section. In contrast to typical homogeneous AEMs, the asymmetric membranes present controlled variations in the functionalization, either in magnitude or in chemical composition, along the thickness of the membrane. Such spatial control is particularly relevant to tailor different properties across the thickness of the membrane, to optimize requirements of the different device electrodes. For instance, by optimizing the distribution of hydrophilic functional groups, it becomes possible to modulate local water uptake and ion conductivity, creating a more favorable hydration profile between the anode and cathode sides. A central parameter in this context is the Degree of Grafting (DoG), which reflects the fraction of grafted chains, in the polymer matrix. The distribution of functional groups bonded to the side chain grafts, introduced during subsequent amination step, directly affects membrane performance, influencing properties such as ion conductivity and water uptake. This distribution is expected to follow the DoG profile, and the successful design and validation of such membranes require reliable methods to determine the local DoG, which is not accessible by standard characterization techniques. The global DoG is usually obtained by gravimetric analysis, although other techniques reported in the literature include electron spin resonance [12], thermogravimetry [13], titration [14], elemental analysis [15], and nuclear magnetic resonance [16,17]. However, none of these methods offer spatially resolved information at micrometer-scale resolution, providing only the global DoG across the membrane. Among these methods, gravimetry is widely recognized as the reference technique for determining the global DoG in grafted polymers, owing to its simplicity, reproducibility, and broad acceptance in the field and it was used in this study as the reference technique. Other approaches, such as ESR, TGA, titration, elemental analysis, or NMR, although reported, are not commonly adopted as standard reference methods for DoG determination.

Spectroscopic methods, such as micro-Raman spectroscopy (MRS) and FTIR, are established tools for assessing chemical modifications in functional membranes. MRS, in particular, is widely available, non-destructive, and capable of producing micrometric maps based on vibrational fingerprints of the base polymer and grafted moieties [18–23]. In analytical chemistry, these spectroscopic techniques are often combined with chemometric strategies to enhance quantitative reliability, but such integration has not yet been explored for DoG mapping. MRS with an analysis ratio between peak height or area (ratiometric) has been quantitatively applied in the context of fuel cell membranes to evaluate grafting [22,23], functionalization levels [21,24], investigate the catalytic layer of catalyst-coated membranes [25], and monitor water and solvent distributions in operando fuel cells [26–30]. FTIR spectroscopy combined with ratiometric methods has also been employed to quantitatively assess the DoG in membranes [16,17,31,32]. Similarly, confocal laser scanning microscopy with

fluorescence detection has been used for quantitative DoG mapping [33–35]. In contrast, techniques based on EDX coupled with SEM have been applied to visualize DoG distribution, but only in a qualitative manner [36–43].

While all the aforementioned techniques provide valuable insights into membrane composition and functionalization, the quantitative analyses reported so far have relied exclusively on ratiometric approaches, such as peak intensity or area ratios. These methods, although practical, make limited use of the full spectral information and are more sensitive to baseline variations and spectral overlaps. From an analytical perspective, this represents a major limitation, as the quantitative robustness and transferability of ratiometric methods are often restricted by experimental artifacts and spectral interferences.

In contrast, multivariate analysis (MVA) of Raman data, especially techniques such as classical least squares (CLS), remains underexplored in the context of membrane characterization. When used, it has been mostly limited to *in operando* studies targeting water and solvent quantification. For example, Scharfer et al. used CLS to investigate water and methane diffusion in Nafion® membranes [26,27], and Götz et al. applied MVA to analyze organic solvents under operando conditions [44]. Thibault et al. employed principal component analysis (PCA), evolving factor analysis (EFA), and multivariate curve resolution (MCR) to study ionic transport and nitrate distribution in Solvay's anion exchange membranes [45]. Such chemometric strategies, however, are well established in analytical chemistry for extracting quantitative information from complex spectra, making their application to AEM characterization a natural yet unexplored extension.

To the best of our knowledge, no previous study has employed multivariate chemometric analysis to evaluate quantitatively the graft distribution in AEMs using MRS. Our approach fills this gap by utilizing CLS decomposition to extract spatially resolved DoG profiles from full spectral data, enabling a more robust and quantitative analysis compared to conventional ratiometric methods.

Furthermore, the obtained spatial signal profile, which is proportional to DoG, must be related to the total measured membrane DoG in order to determine the proportionality constant. However, this is not a trivial task, taking into account that the membrane expands locally as the graft is incorporated. To the best of our knowledge no solution has been proposed in the literature; instead, the average DoG measured along the membrane thickness has been used to obtain the proportionality constant in refs [33–35]. We developed a model to account for this effect, which enabled us to relate the DoG-proportional profile to the overall measured DoG, as well as evaluated the error with relation to the use of the simple average. This modeling step was essential to overcome the non-uniformity of the reference membranes, a limitation intrinsic to grafted systems, and to ensure that the local Raman signal could be consistently related to the gravimetric DoG, the established reference method.

Herein, we introduce for the first time a Raman-based chemometric approach for determining local DoG profiles with spatial resolution.

MRS was selected as the core characterization technique due to its submicrometric spatial resolution and its high chemical sensitivity and selectivity toward both the base polymer and the grafted material. These features enable fast, non-destructive analysis of local chemical composition along the membrane cross-section, which is essential for resolving through-thickness DoG gradients. In addition, Raman spectroscopy allows direct probing of the polymer backbone and grafted functional groups without the need for labels or extensive sample preparation. Additionally, its wide availability in laboratories worldwide further makes it a practical and versatile technique for determining local DoG profiles in grafted polymer membranes. The method employs CLS fitting to deconvolute Raman spectra into contributions from the base polymer and grafted chains. By calibrating the CLS scores against bulk DoG values, we establish a proportional relationship that enables local quantification of the grafted mass fraction at each point across the membrane cross-section. The approach is validated on membranes with

known DoG and then applied to asymmetric membranes to extract local grafting profiles. Furthermore, this technique is broadly applicable to any grafted copolymer system with side-chain functionalization, extending its potential beyond the specific membranes studied here. In this work, the gravimetric DoG values were therefore employed as reference for the calibration of the Raman-based chemometric model, while a mathematical correction was introduced to account for the local expansion of the membrane during grafting. By applying established chemometric techniques to extract quantitative information from Raman spectra, this work positions the methodology within the framework of analytical chemistry, emphasizing method development, validation, and robust data interpretation.

This technique opens a new pathway for rapid, accessible, and non-destructive quantification of graft distribution in functional membranes using standard MRS equipment. It is particularly valuable for the development of the novel asymmetric AEMs, where precise control and measurement of local functionalization are crucial for performance optimization.

2. Theoretical background

2.1. Classical least squares (CLS) model

CLS is a multivariate analysis technique in which each measured Raman spectrum is expressed as a linear combination of the contributions from pure components. In the present system, these components correspond to the base polymer and the grafted side chains. The CLS model provides **scores** (S_i) for each component i , which are representative of their contributions to the measured spectrum.

The loadings were obtained by measuring the spectra from isolated compounds, and calibration is required to relate scores to actual concentrations.

The DoG is defined as the mass ratio of the grafted polymer (m_G) to base polymer (m_B):

$$DoG = 100 \cdot \frac{m_G}{m_B} \quad (1)$$

For a uniform sample of grafted polymer, the ratio SR between the scores of the grafted chains (S_G) and the base polymer (S_B) is proportional to the DoG, as described in Appendix A.

$$SR = \frac{S_G}{S_B} \propto DoG \quad (2)$$

Taking into account that the MRS evaluates only a small portion of the sample, which can be considered homogeneous at this scale and representative, it is possible to conduct a direct application in determining the local DoG of a non-homogeneous sample.

2.2. DoG-proportional swelling model to correlate local SR and SR_{Tot}

The DoG is defined as the ratio between the mass of grafted polymer and the mass of the original polymer matrix. Although this definition is conceptually simple, accurately measuring the true DoG, particularly its spatial distribution within the membrane, is quite complex. The most widely employed method is gravimetric, where the DoG is calculated from the mass difference before and after grafting. This provides a global value, representing the overall modification of the membrane, without spatial resolution.

Once a linear relationship between the volumetric concentration of grafted polymer and the Raman-derived SR is assumed, as derived as described in the previous section, establishing a calibration curve between SR and the overall measured DoG requires a set of samples with homogeneous grafting. However, due to the diffusion-limited nature of the grafting process, dominated by the transport of VBC monomer into the membrane, obtaining uniformly grafted samples is extremely difficult. Consequently, the DoG exhibits spatial variation along the

membrane thickness, leading to a fundamental limitation: local SR profiles are measured via MRS while only global DoG values are accessible from gravimetry. This mismatch arises due to the local information obtained from MRS corresponding to a **volumetric concentration of grafted polymer**, while the global DoG is defined as a **mass fraction relative to the original membrane**. Furthermore, as grafting progresses, the membrane undergoes significant volume expansion, and this expansion is non-uniform: regions with higher grafting swell more than regions with lower grafting. This non-uniform expansion makes it even more difficult to associate directly local MRS data with the global DoG [16,17].

To overcome this limitation, a **DoG-proportional swelling model** was developed to link the local $SR(z)$ profiles measured by MRS to the global DoG obtained gravimetrically. The model assumes that the membrane expands volumetrically in proportion to the local degree of grafting, characterized by a proportionality constant α :

$$dV(z) = dV^0 [1 + \alpha DoG(z)], \quad (3)$$

where $dV(z)$ represents the local volume after the grafting at a given coordinate z and dV^0 corresponds to the corresponding volume before swelling.

Since the $SR(z)$ profiles are measured, we define $\tilde{\alpha}$ as the equivalent proportionality constant in terms of SR, once SR is assumed to be proportional to DoG:

$$dV(z) = dV^0 [1 + \tilde{\alpha} SR(z)] \quad (4)$$

The value of $\tilde{\alpha}$ is determined by numerically solving Eq. (5) and the total score ratio SR_{Tot} can then be determined by solving Eq. (6). This approach provides a more physically accurate estimation of the global DoG based on the local MRS profiles rather than simply considering the average SR along the z -axis:

$$\frac{t^0}{E_s} = \int_0^{t'} \frac{dz}{1 + \tilde{\alpha} SR(z)} \quad (5)$$

and

$$SR_{Tot} = \frac{\int_0^{t'} \frac{SR(z) \cdot dz}{1 + \tilde{\alpha} SR(z)}}{\int_0^{t'} \frac{dz}{1 + \tilde{\alpha} SR(z)}}, \quad (6)$$

where t^0 and t' are the initial and final membrane thicknesses, respectively, and E_s is the surface expansion of the membrane (ratio between final and initial surface areas of the membrane). Full derivation of Eq. (5) and Eq. (6) can be found in Appendix B. The expression for SR_{Tot} can be interpreted as a weighted average of $SR(z)$, with weights $w = (1 + \tilde{\alpha} SR(z))^{-1}$. For $\tilde{\alpha} = 0$, Eq. (6) is reduced to the continuous arithmetic mean of $SR(z)$ along the membrane thickness.

2.3. Comparison between the dog-proportional swelling model and the simple average

To investigate the impact of using the arithmetic mean of $SR(z)$ instead of the DoG-proportional swelling model, we conducted a theoretical analysis to estimate the maximum possible error arising from this simplification. The goal was to identify the conditions in which the simple averaging approach may still be valid and to quantify the associated errors. This is particularly relevant for experimental workflows, where a simple procedure may be preferred, providing that the induced error remains below the typical experimental uncertainty. A full derivation of the maximum error and boundary conditions considered in this model is shown in Appendix C. To assess the magnitude of this error, a worst-case scenario was identified: a stepwise profile with two regions of equal thickness ($F = 0.5$), one with $SR = SR_{min}$ and the other with $SR = SR_{max}$. Among all possible profiles bounded between SR_{min} and SR_{max} , this configuration produces the **maximum relative error** between the

average SR and the DoG-proportional swelling model DoG SR_{Tot} :

$$\begin{aligned} \text{Error} &= \left| \frac{\text{mean}(SR) - SR_{Tot}}{SR_{Tot}} \right| \times 100 < \text{Error}_{\max} (\%) \\ &= \left| \frac{\text{mean}(SR_{\text{step}}) - SR_{\text{step}, Tot}^{\tilde{\alpha}}}{SR_{\text{step}, Tot}^{\tilde{\alpha}}} \right| \times 100 \end{aligned} \quad (7)$$

where SR_{step} is the SR of the step configuration and $SR_{\text{step}, Tot}^{\tilde{\alpha}}$ is the total SR of the step profile calculated with a given value of $\tilde{\alpha}$. This error limit is independent of the specific shape of the $SR(z)$ profile, including continuous ones, as introducing more transitions (or even smooth variations) always reduces the deviation from the true SR_{Tot} . Thus, the degenerate $F = 0.5$ case establishes a practical upper bound for the error when using the arithmetic mean instead of the full volumetric model. One important simplification obtained by this rise step model is the fact that the $\text{Error}_{\max}$ depends only on $\tilde{\alpha}$ and $r = SR_{\max} / SR_{\min}$.

Fig. 1. plots the maximum error as a function of r for different values of $\tilde{\alpha}$ between 0.2 and 1, offering a straightforward way to estimate the upper bound of the deviation without requiring full integration. Notably, for $\tilde{\alpha} = 0.35$, corresponding to the ETFE/VBC system (as determined in the next section), and $r < 2$, the maximum error is less than 4% if the arithmetic average is used to estimate SR_{Tot} , however, if more modest values of $r < 1.5$ are considered, then less than 1.5% error is expected.

Notably, this modeling approach is not limited to MRS due to the need to compensate for the expansion, which is not a MRS measurement-related problem, but a question inherent to the grafting process that will imply applying the correction to measurements by any technique, unless the absolute mass results are provided instead of concentrations. Therefore, this model is broadly applicable to any technique that produces a depth-resolved signal proportional to volumetric concentration, including confocal fluorescence microscopy, X-ray photoelectron spectroscopy (XPS), and EDX mapping. Depending on the sensitivity and noise level of the experimental method, the arithmetic mean may still be acceptable, particularly when the estimated error is below the typical measurement uncertainty. Alternatively, the integral formulation can be used to correct for expansion-induced distortions more precisely.

3. Materials and methods

3.1. Preparation of symmetric and asymmetric-grafted films

The **symmetric** ethylene tetrafluoroethylene (ETFE)-grafted membranes with different DoGs were prepared by RIG. Commercial ETFE films with a thickness of 50 μm were supplied by Nowofol. Then, ETFE films ($13 \times 8 \text{ cm}^2$) were pre-irradiated under air atmosphere at low temperature (-10°C), following procedures previously reported in the literature [19,40,46]. The pre-irradiation was performed using a

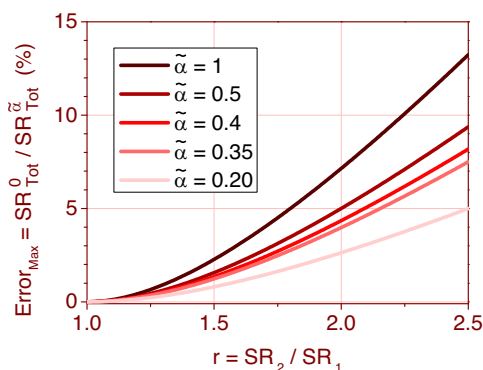


Fig. 1. Maximum error for SR_{Tot} when considering the average of $SR(z)$ as a function of SR_2/SR_1 for different values of $\tilde{\alpha}$.

Dynomiton Continuous Electron Beam Unit from Radiation Dynamics Inc. (USA), model DC 1500/25/4 – JOB 188. The absorbed dose was controlled by adjusting the number of passes under the electron beam, with each pass delivering 5 kGy. The beam energy used was 0.55 MeV, and the current was 2.87 mA. Immediately after irradiation, the films were stored at -40°C in air until the grafting procedure was conducted.

For the grafting step, the pre-irradiated ETFE films were placed in a glass reactor containing a grafting solution composed of 10% (v/v) 4-vinylbenzyl chloride (VBC, 90%, Sigma-Aldrich, inhibitor-free) in isopropanol. The solution was previously deoxygenated by purging with nitrogen (N_2) for 1 h. The reactors were then sealed and maintained under constant stirring at 70°C for 4 h. After the reaction, the grafted films were thoroughly washed with toluene and acetone to remove residual homopolymer and then dried in a vacuum oven at 50°C for 16 h. The DoG was determined gravimetrically. A graph showing the relationship between absorbed dose and the resulting degree of grafting (DoG) is provided in the Supporting Information (Fig. S1). The seven grafted films used in this study presented DoG values of 13 p.p., 31 p.p., 49 p.p., 51 p.p., 75 p.p., 82 p.p. and 110 p.p. corresponding to absorbed doses of 5, 10, 15, 25, 50, 35, and 75 kGy, respectively. To avoid misunderstandings with other percentage terms, through this work we refer to DoG as percentage points (p.p.) instead of percentage, with a 1 to 1 correspondence (e.g., 30 p.p. instead of 30%).

To demonstrate that our Raman chemometric approach is capable of differentiating the grafting level across the sample thickness, an **asymmetrically** ETFE-grafted film was synthesized. For this purpose, a pre-irradiated ETFE film (100 kGy) was positioned between the two compartments of a custom-designed reactor and sealed with o-rings. One compartment was filled with a VBC solution with a concentration of 60% (v/v, in isopropanol), while the other one was filled with a 10% (v/v, in isopropanol) VBC solution. Both solutions were deoxygenated by purging with N_2 for 30 min. The reactor was then sealed and maintained at 70°C for 4 h to simulate the same grafting conditions applied to the previously described samples. After the grafting process, the asymmetrically ETFE-grafted film was thoroughly washed with toluene and acetone and then dried in a vacuum oven at 50°C for 16 h. All samples presented in this study were characterized by Fourier transform infrared (FTIR) spectroscopy and the degree of crystallinity of samples were obtained by x-ray diffraction (XRD).

3.2. Determination of the reference DoG of the membranes

The reference technique used to obtain the DoG of the membranes along this work was gravimetric, since it is recognized and widely reference method for measuring DoG.

The DoG was determined gravimetrically by comparing the mass of the grafted films to that of the original ETFE films, using Eq. 8.

$$\text{DoG} = \frac{W_f - W_i}{W_i} \times 100\%, \quad (8)$$

where W_f is the ETFE-grafted film weight, and W_i is the initial weight of ETFE.

3.3. Fourier transform infrared (FTIR)

Fourier transform infrared (FTIR) spectra of samples were collected using a Bruker INVENIO S spectrophotometer in an attenuated total reflection (ATR) mode at a frequency range of $4000\text{--}400 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} and 64 scans. The spectra are normalized to the ETFE backbone band at 1325 cm^{-1} .

3.4. X-ray diffraction (XRD)

The crystallinity of the samples were estimate by X-ray diffraction (XRD) using a Rigaku miniflex-II X-ray diffractometer with $\text{Cu-K } \alpha$

radiation source ($\lambda = 1.5409 \text{ \AA}$), voltage of 30 kV, current of 15 mA, step of 0.02° and scanning rate of 1° min^{-1} . The data were collected in the range of 2θ from 5 to 30° . Fityk software was used for fitting curves and data analysis and the degree of crystallinity (X_c) was calculated by Eq. 9.

$$X_c = \frac{A_{\text{crystalline}}}{A_{\text{crystalline}} + A_{\text{amorphous}}}, \quad (9)$$

where $A_{\text{crystalline}}$ is the area under the crystalline peaks and $A_{\text{amorphous}}$ is the area under the amorphous halo.

3.5. Section preparation

In the literature, confocal spectroscopy is currently used to assess properties across the membrane thickness, in which the typical approach involves focusing the laser beam through the membrane depth [16,17,21,24,26,27,40,44,45]. This method has the advantage of requiring minimal sample preparation; however, it also presents several drawbacks. These include the need for wavelength-dependent Beer–Lambert law corrections due to light absorption, spherical aberrations at the sample interface, and limited depth resolution. The latter arises due to the focal depth in air being already in the micrometer range and suffering further increase by the membrane's refractive index and the lower numerical aperture (NA) in the medium [47]. These optical limitations apply broadly to polymeric ion-exchange membranes, such as AEM and proton-exchange membranes (PEM) types, regardless of the specific functional group, since they stem primarily from refractive and geometrical constraints. Moreover, when measurements are performed with membranes immersed in liquids, it is often necessary to develop strategies to determine the start and end points of the membrane. This is especially challenging when the refractive indices of the membrane and the surrounding medium are similar, preventing clear detection of interface reflections. Since our measurements were not performed in operando conditions, it was unnecessary to apply depth profiling via laser focusing. Instead, we opted to acquire Raman spectra along the cross-section of physically cut membrane samples. This approach requires only minimal sample preparation, which is fast, straightforward, and not labor-intensive. Importantly, it offers several advantages: clear visualization of membrane boundaries, higher spatial resolution across the thickness, and reduced complexity in data processing as well as no optical corrections were needed beyond standard baseline correction.

The grafted membranes were cut into pieces of approximately $10 \times 10 \text{ mm}^2$ and mounted on a custom fixture designed to expose their cross-section, as illustrated in Fig. 2a. The fixture consisted of a holder for two microscope slides with ground edges (Knittel, Germany), each featuring a small chamfer of approximately $0.3 \text{ mm} \times 45^\circ$ at the edges. This chamfer ensured that the tip of the membrane remained free from contact with the glass, thereby preventing interference from Raman signals originating from the glass slides. The membrane was sandwiched between the two slides, leaving a small portion of approximately 1 mm protruding from the edges. It was then secured in place using fixture

plates. A microtome blade was used to trim the exposed edge of the membrane, creating a clean cross-sectional surface, as shown in Fig. 2b. Representative optical microscope images of the exposed membrane cross-sections after cutting are shown in the Supporting Information (Fig. S2) to illustrate the quality of the preparation. This setup allowed for the measurement of section planes aligned with the xy-plane of the MRS system. Along the work we defined the z axis as aligned with the membrane's depth, as indicated in Fig. 2c, instead of aligned to the beam propagation direction since we mostly refer to the membrane dimensions much more than to the beam depth along the work.

3.6. MRS mapping

MRS mappings were acquired using an Xplora Raman system (Horiba, France) equipped with a 785 nm laser, a $50\times$ ($\text{NA} = 0.5$) objective, and a $600 \text{ grooves-mm}^{-1}$ diffraction grating. Linear (1D) maps along the z-axis were acquired with 1 s acquisition time per point and a single accumulation. Both 100-point and 200-point scans were acquired. For each membrane, three 100-point linear maps were used for calibration purposes. These measurements were taken along the same $\sim 1 \text{ cm}$ long cross-section of the membrane, with three linear scans acquired: one near the center and one near each end of the cross-section to assess the **within-section reproducibility** of the method. An additional 200-point map was acquired along the same cut and subsequently used for validation. For reproducibility assessment across different membrane regions, additional maps were acquired in multiple cross-sections, as detailed in the Results section.

3.7. Data processing

CLS was performed utilizing the MVA software package developed by Eigenvector research, Inc. (Wenatchee, USA), embedded within Horiba's LabSpec software. Spectra were acquired from 135 cm^{-1} to 2574 cm^{-1} but only the 240 cm^{-1} – 1800 cm^{-1} region was used for optimal baseline correction. This range included the main peaks of interest while avoiding wide baseline-dominated regions that could bias the least squares fitting. Spikes due to cosmic rays were manually identified and removed. A 4th-degree polynomial baseline was subtracted from all spectra.

The MRS profiles were measured starting and finishing at $\sim 2 \text{ }\mu\text{m}$ before the limit of the membrane to avoid measuring points too close to the edges. Severe changes in baseline were observed at these limits, causing difficulties when applying uniform baselines along the data set. Aiming to calculate the total SR, depending on the values along the whole membrane thickness as described in (section 2.6), two more points were added to the SR profile at the positions corresponding to the extremities, repeating the first or last SR value.

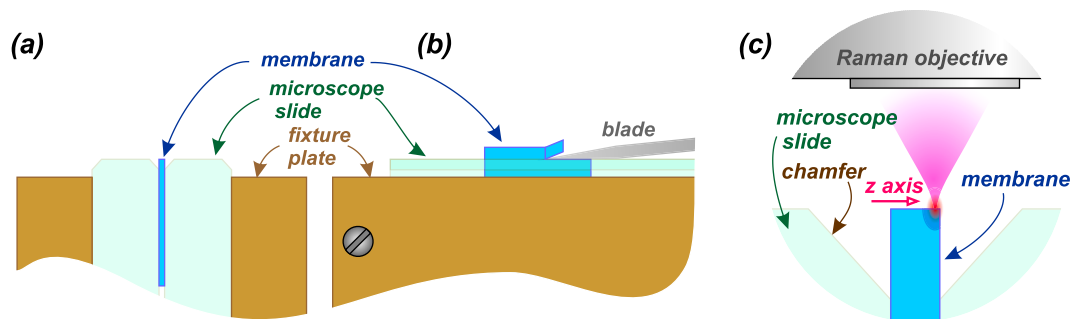


Fig. 2. Scheme of the assembly used for exposing the membrane's cross-section. (a) Transversal (cross-sectional) view of the setup. (b) Side view of the assembly illustrating the trimming of the membrane. (c) Magnified view of the exposed membrane section after cutting. The direction of the z axis is indicated in (c).

3.8. Loadings

For the CLS analysis, spectral loadings for both ETFE and VBC were required. The ETFE spectrum was obtained directly from a pristine ETFE membrane. However, a reference sample for VBC was not available. To overcome this, the VBC spectrum was estimated by spectral subtraction. A grafted-ETFE membrane was measured in a region with high DoG, and then, the reference spectrum was carefully subtracted from this spectrum, in small percentage steps, while monitoring the attenuation of ETFE characteristic peaks. A fine spectral alignment in the Raman shift axis was also performed to correct for small calibration differences between the two measurements, which were acquired at different times and can lead to errors in the final MVA analysis [48]. The spectrum was shifted by fractions of cm^{-1} , and subtraction was repeated until the derivative-shaped residuals, indicative of minor peak misalignments, were minimized, ensuring accurate spectral subtraction. Once satisfactory subtraction and alignment were obtained, the resulting spectrum was baseline-corrected and employed as the VBC loading. The spectra for pristine ETFE, the grafted membrane, and the resulting VBC spectrum are shown in Fig. 3.

Alternative approaches were also investigated for obtaining the VBC loading spectrum, including measuring poly(VBC) precipitated from the grafting solution, and using reference spectra available through the KnowItAll® software (Mendeley signature database). However, the subtracted spectrum provided significantly superior results in terms of spectral fitting and model performance. Furthermore, the ideal condition is to acquire the reference loading spectra using the same instrument, or at least a spectrometer with similar optical characteristics. Although spectral correction can be applied by calibrating against a standard light source and Raman shift correction can be performed using references, such as silicon or mercury lamps, differences in gratings, spectrometer arms, and slit widths can affect the spectral sampling. This may lead to discrepancies in peak intensities, especially for sharp bands, which can be oversampled or undersampled depending on the instrument configuration.

Prior to applying CLS, the loadings were normalized. The CLS scores s_i were then converted into normalized scores S_i , such that their sum for each spectrum equaled 100%:

$$S_i = 100 \cdot \frac{s_i}{\sum s_j} \quad (10)$$

This normalization is not necessary, taking into account that the normalization factor cancels out when considering the SR. However, the use of the normalized score allowed us to keep only the VBC score map S_{VBC} for each measurement, since it is possible to recover the ETFE score S_{ETFE} and $\text{SR} = S_{\text{VBC}}/S_{\text{ETFE}} = S_{\text{VBC}}/(100 - S_{\text{ETFE}})$.

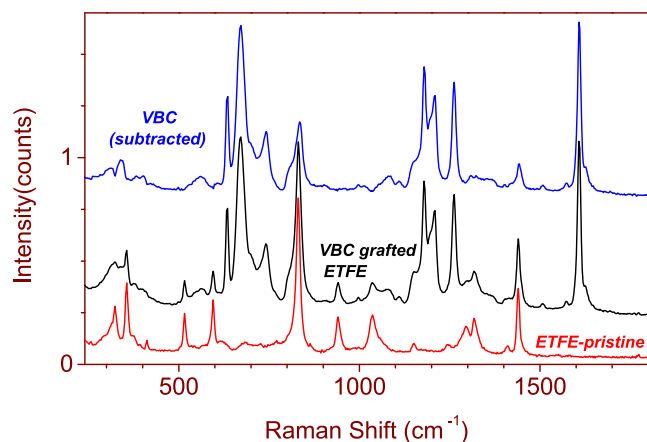


Fig. 3. Reference Raman spectra. Measured spectra from pristine ETFE and grafted VBC-ETFE membranes and VBC spectrum obtained after subtraction.

To account for small calibration differences between the measured and loadings spectra, a post-CLS spectral alignment was performed. The Raman shift axis of all spectra in the mapping was adjusted by small fractions of wavenumbers (cm^{-1}), minimizing the overall CLS residual error. This shift optimization was confirmed by the reduction of peak-like features in the residual spectra. After alignment, the final CLS residual errors ranged from 0.2% to 0.4%. The residual spectra were dominated by random noise, with only minimal and occasional signals near 833 cm^{-1} and 1620 cm^{-1} , typically at the edges of these peaks. Sample spectra and their residuals are shown in Fig. 4. The low residuals and absence of structured features indicated that the spectral decomposition using the selected loadings provided an excellent fit to the measured data. Additional CLS decomposition results for membranes with different DoG levels, both at the center and near the surface, are presented in the Supporting Information (Fig. S3).

It should be noted that the present multivariate model was developed using membranes with comparable graft architectures, and therefore its sensitivity is primarily directed toward variations in DoG rather than subtle microstructural differences such as graft chain length or branching, which are expected to manifest as very subtle differences in spectra.

3.9. Numeric evaluation of integrals and zero of functions

The volumetric expansion coefficient (α) was obtained numerically by solving the integral Eq. (5) using MATLAB's fzero function, which combines bisection, secant, and Brent's methods to find the root of nonlinear equations. The integrals in Eq. (5) and Eq. (6) were evaluated using the trapezoidal rule.

3.10. Calibration and validation

Calibration was performed by comparing the gravimetrically measured overall DoG of the membranes to the total SR of the profiles SR_{Tot} .

Validation of the calibration curve was performed by acquiring a second independent MRS mapping dataset. This map, consisting of 200 points, was measured at a different position along the same transversal cut used in the calibration. The data were processed using the same CLS loadings and normalization procedures. The resulting SR profile was used to compute the predicted overall DoG through the volumetric expansion model (Appendix B), using the same value of α obtained during calibration.

To assess the performance of the model, parity plots were generated

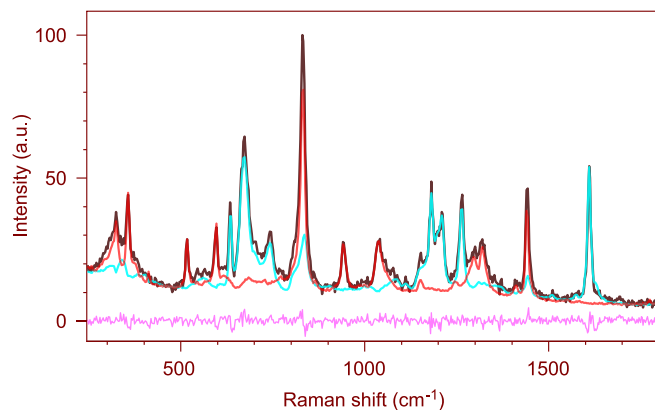


Fig. 4. CLS decomposition. Example of loadings decomposition and residual obtained after CLS operation at a spectrum point for a 31p.p. grafted membrane. Black line: measured spectrum; Ciano: VBC loading multiplied by the corresponding score; Red: ETFE loading multiplied by the corresponding score; Magenta: residual after subtraction of the VBC and ETFE score multiplied loads from the measured spectrum.

comparing predicted and measured DoG values. Statistical metrics, such as the coefficient of determination (R^2), root mean square error of prediction (RMSEP), and both absolute and relative errors, were calculated. These metrics were used to evaluate the accuracy of the model in capturing the relationship between local Raman-derived SR profiles and the global DoG.

Even though a calibration and validation procedure was adopted, it is important to emphasize that the objective of the curve is to prove the linear relationship between the DoG and the normalized SR, not to determine the DoG itself. In this situation, the calibration/validation would be mandatory. Once the relationship was proven, its coefficient was taken to obtain the DoG distribution along the membrane's cross-section by multiplying the SR by the graphically obtained coefficient. By doing this, the sample DoG transversal profiles for all samples were obtained.

4. Results and discussion

4.1. FTIR

The functional groups of the ETFE-grafted molecular structure were identified by FTIR spectroscopy Fig. 5 to confirm the synthesis. In Fig. 5, the filled spectrum corresponds to the pristine ETFE structure, and the bands at 1450, 1325, 1252, and 1116 cm^{-1} are assigned to the CH_2 scissoring mode, CH bending mode, CH_2 bending mode, and CF stretching mode, respectively [49–51]. After the grafting process, the presence of poly(VBC) grafts in the molecular structure is evidenced by the band at 824 cm^{-1} , which is associated with the out-of-plane bending mode of the benzyl ring groups [49]. It can be observed that the intensity of this band increases with increasing degree of grafting. Table 1 summarizes the FTIR bands and the corresponding vibrational mode assignments.

4.2. Comparison with reference overall DoG samples

Before calculating the SR_{Tot} , it is necessary to determine the expansion factor α , which is then used in Eq. (6). This factor is expected to be constant for a given material, assuming that membrane expansion is directly proportional to DoG. To evaluate whether α is indeed homogeneous across samples, we analyzed the dimensional changes of the membranes as a function of DoG. Fig. 6a shows the measured expansion

Table 1

FTIR Band assignment and mode descriptions for samples.

Band	Mode descriptions	Ref.
1450 cm^{-1}	sc(CH_2)[bkb]	[49,50]
1325 cm^{-1}	$\delta(\text{CH})$	[49,51]
1252 cm^{-1}	$\delta(\text{CH}_2)$	[49,51]
1167 cm^{-1}	$\delta^{\text{ip}}(\text{CH})[\text{ring}] + \nu(\text{CC})[\text{bkb}]$	[49,50]
1116 cm^{-1}	$\nu(\text{CF})$	[49,51]
1046 cm^{-1}	$\{\nu(\text{CC}) + \nu(\text{CF}) + \delta(\text{CH})\}[\text{bkb}]$	[49,51]
972 cm^{-1}	$\delta^{\text{oop}}(\text{CH})$	[49]
824 cm^{-1}	$\delta(\text{CH})^{\text{oop}}[\text{ring}]$	[49]
744 cm^{-1}	$\delta(\text{CH})^{\text{oop}}[\text{ring}] + \delta(\text{CCC})^{\text{ip}}[\text{ring}] + r(\text{CH}_2)[\text{bkb}]$	[49]
667 cm^{-1}	$\delta(\text{CCC})^{\text{ip}}[\text{ring}]$	[49]

ν – stretching; δ – bending; r – rocking; sc – scissoring; ip – in-plane; oop – out-of-plane; ring – vibration involving phenyl ring; bkb – vibration localized mainly on the carbon chain representing the polymer backbone.

in surface area (from dimensional measurements), thickness (from micrometer measurements), and the calculated volumetric expansion. The data suggest anisotropic expansion: both surface and thickness increase similarly, whereas isotropic expansion would predict a larger increase in surface area relative to thickness. Additionally, while volumetric expansion increases linearly with DoG, the ratio between surface and thickness expansions is unstable at lower DoG values (<50%). For clarity, we reiterate that all DoG values presented are expressed in percentage points (p.p.), with a 1:1 correspondence to percent (e.g., 30 p.p. = 30%). This notation aims to distinguish DoG from other percentage-based quantities discussed in this section.

As shown in Fig. 6c, membrane density decreases from the pristine ETFE value toward that of poly(VBC), stabilizing at ~80% of the original density beyond 50% DoG. The density was calculated by using the DoG and the volume expansion values via $\rho = \frac{m_f}{V_e} = \rho_0 \frac{\text{DoG}+1}{V_e+1}$, where ρ_0 is the initial density, $V_e = \frac{V_f}{V_0} - 1$ is the volumetric expansion, and $m_f = m_0(\text{DoG} + 1)$. The density trend is consistent with the progressive reduction in degree of crystallinity, obtained by XRD measurements, induced by grafting process (see Fig. S5). Pristine ETFE exhibits a crystallinity of 50%, which decreases sharply upon grafting, reaching values in the range of 20–32% for grafted membranes. For DoG values above approximately 50%, the crystallinity stabilizes around ~22%, in agreement with the trend observed in density values. These results indicate that the density evolution with DoG reflects both the increase in grafted content and the concomitant reduction and stabilization of the crystalline fraction within the membrane series.

To estimate α for each membrane, Eq. (5) was solved numerically using the measured SR profile, original thickness, and macroscopic surface expansion. The resulting α values are plotted in Fig. 6d. A green line represents the expansion factor calculated directly from dimensional data (dashed line in Fig. 6a), scaled by the SR-to-DoG proportionality constant (determined later in the manuscript). For membranes with DoG >50 p.p., the computed α aligns closely with this reference. At lower DoG, however, α is smaller. This suggests that α may not be constant across all DoG values. One possible explanation comes from the fact that grafting occurs in discrete domains: at lower DoG levels, grafted domains begin to form within a matrix that remains mostly pristine. As these grafted regions grow in mass and attempt to expand, their deformation is constrained by the surrounding ungrafted material, limiting the observed expansion coefficient. As DoG increases and the volume fraction of grafted regions grows, mechanical resistance is gradually overcome by the expansion forces, eventually reaching the yield strength of the material and leading to an expansion equilibrium. Although this interpretation, involving constrained swelling for low DoG due to isolated grafted domains, is not widely discussed in the literature, it provides a plausible explanation for the observed behavior and is supported by our data. This means that the expansion coefficient α is influenced by internal mechanical constraints with lower influence of intrinsic to the material's chemistry, although the intrinsic properties

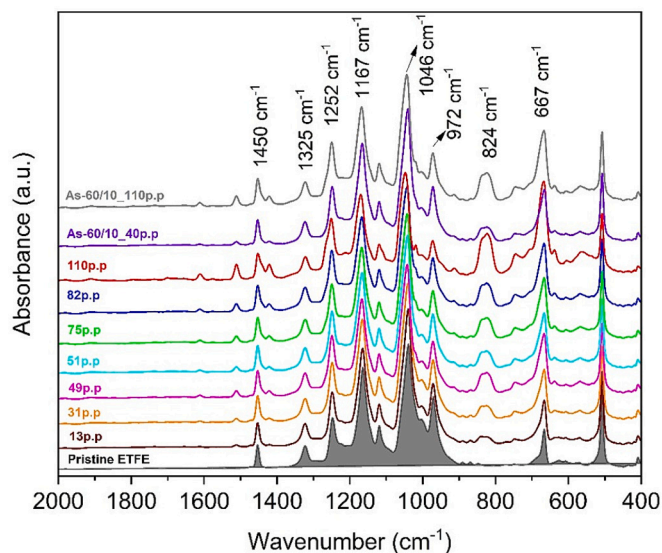


Fig. 5. FTIR. ATR spectra of pristine ETFE, symmetric ETFE-g-VBC films, and asymmetric ETFE-g-VBC (As-60/10, both sides). The spectra are normalized to the polymer backbone band at 1325 cm^{-1} .

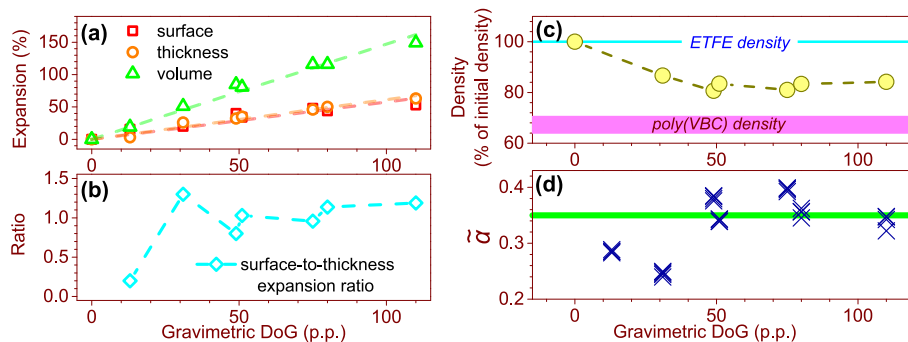


Fig. 6. Membrane expansion, calculated densities, and derived volume expansion coefficients. Measured membranes' expansion and linear fits (a), surface to thickness expansion ratio (b) and corresponding calculated densities (c). (d) Calculated $\tilde{\alpha}$ values from the SR profiles. Green line in (c) represents the volume expansion coefficient obtained from the membrane's measured volumetric expansion from the green curve in (a). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of the material are crucial to the corresponding physical properties of materials. The simple model used in this work, which assumes a constant proportionality between DoG and expansion, could be improved by incorporating a DoG-dependent $\tilde{\alpha}$, which accounts for these internal forces.

Although the value of the constant of proportionality between SR and DoG is presented later in this section, we introduce the DoG values preliminarily to assess whether a constant $\tilde{\alpha}$ is appropriate within each calibration membrane. Fig. 7 presents Jittered scatter plot of local DoG values from reconstructed profiles, allowing us to assess whether each membrane falls predominantly within a single expansion regime. No overlap near the ~ 45 p.p. threshold is observed, supporting the assumption of a constant $\tilde{\alpha}$ within membranes individually. However, this does not preclude a nonlinear relationship between $\tilde{\alpha}$ and DoG when considering a wider grafting range.

For asymmetric grafted membranes, where the local DoG ranges from a few percent to over 100 p.p., two expansion regimes may coexist within a single sample. This increases uncertainty in DoG profile reconstruction, as the current model does not account for $\tilde{\alpha}$ variation with DoG. Although our data suggest that $\tilde{\alpha}$ increases from ~ 0.25 to ~ 0.35 around the 50 p.p. DoG threshold, limited data and lack of direct stress/strain measurements hinder a more detailed characterization. The next step would be conducted to define a piecewise or continuous function $\tilde{\alpha}(\text{DoG})$, either empirically or through mechanical modeling. Nonetheless, within the calibration range, assuming a constant $\tilde{\alpha}$ remains a reasonable and useful approximation that captures the key behavior observed in the membranes. Furthermore, Fig. 1. indicates a small sensitivity in error for $\tilde{\alpha}$ between 0.25 and 0.35.

It is worth noting that, although $\tilde{\alpha}$ is derived from local SR profiles,

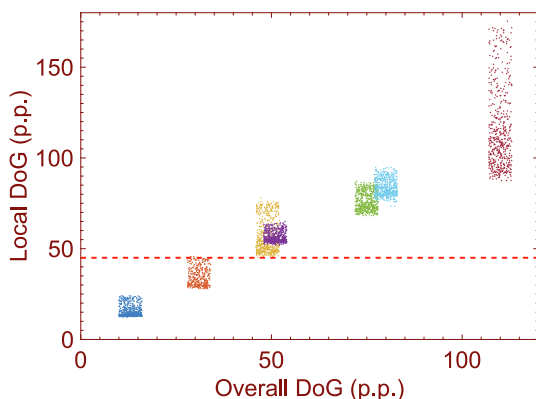


Fig. 7. DoG ranges for the different membranes. Jittered scatter plot for the local DoG measured at the reference membranes. Horizontal line at DoG = 45 p.p. indicates the possible limit for different regimes of the expansion factor $\tilde{\alpha}$.

the area expansion used in its calculation is based on macroscopic measurements, and the membrane thickness used to compute local DoG is also measured macroscopically (e.g., with a micrometer). Thus, both components of the swelling model inherently incorporate bulk expansion. The agreement between the global expansion factor $\tilde{\alpha}_{\text{macroscopic}} \approx 0.35$ and the upper values of local $\tilde{\alpha}$ supports the model's validity, even amid dispersion and resolution limits around DoG ≈ 50 p.p. This suggests that the apparent continuity in volumetric expansion may arise from bulk averaging effects, without ruling out a transition in $\tilde{\alpha}(\text{DoG})$ that remains experimentally unresolved.

The SR profiles measured on all membranes, comprising the three 100-point profiles and the 200-point profile acquired at each membrane section, are plotted as a function of the thickness coordinate z (with $z = 0$ set at the center of the profiles) are shown in Fig. 8, in which all the measured profiles are overlapped. The curves display higher SRs as measured DoG increases, as expected. The increase in membrane thickness with growing DoG is visible. Importantly, the four profiles acquired from different positions of the same cross-section show very similar trends, indicating good **within-section reproducibility** of the method. This is particularly evident from the close overlap of the point clouds, which suggests that the CLS-derived SR values are robust against local variations in sampling. The dispersion of the points also increases along with DoG, which is consistent with the higher signal intensity and membrane expansion at higher grafting levels. Two-dimensional DoG maps acquired over membrane cross-sections are also available in the Supporting Information (Fig. S4), complementing the one-dimensional profiles discussed here.

4.3. Calibration and error analysis

The calibration curve is displayed in Fig. 9a. In this plot, three SR_{Tot}

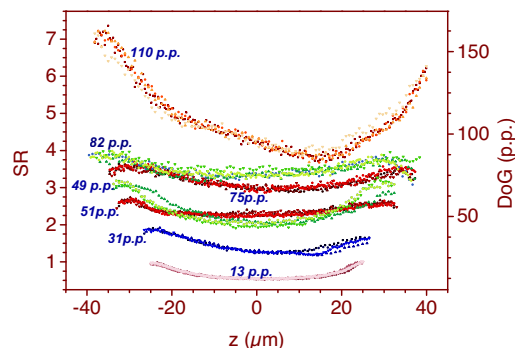


Fig. 8. Measured SR profiles. Measured SR along the membranes thickness z (left axis) and corresponding obtained local DoG (right axis). The gravimetrically measured DoG of the membranes is indicated close to the curves.

values calculated from the 100-point profiles for each membrane were used as calibration points. A linear fit without a linear coefficient was applied to the data. Good adjustment to the line was obtained with $R^2 = 0.9981$. The angular coefficient was then utilized to obtain DoG profiles from the SR profiles, which are shown on the right axis of Fig. 8. The reproducibility within each membrane section was very good, with a standard deviation below 2% (see also Figure 10b, discussed in the next section).

To compare the DoG-proportional swelling model with the simplified average SR taken along the membrane thickness, the SR_{Tot} of Eq. (6) was compared to the average SR as shown in Fig. 10a. The error between the SR_{Tot} and the standard deviation between different measurements taken on the samples, along with the maximum error $Error_{max}$ calculated for the step profile based on the SR range and $\bar{\alpha}$ (Eq. (6)), was considered. In Fig. 10b, the evaluated error is plotted against the standard deviation, where it is noted that, except for the DoG = 110 p.p. sample, the error remains smaller than the standard deviation.

In Fig. 10c, the error normalized by the $Error_{max}$ is plotted, showing that for all the SR profiles, the error was less than 45% in relation to $Error_{max}$. From this data, we can infer that the use of the simplified average value can present a slight effect on the calibration curve. Indeed, in Fig. 9b, a calibration curve is shown to provide $R^2 = 0.9981$ and an angular coefficient compatible with the one obtained with the full integral within only one standard deviation.

We further present in Fig. 11a, the DoG $_{Tot}$ error divided by the average DoG, calculated with the SR profiles of Fig. 8. As $\bar{\alpha}$ increases, the ratio deviates more significantly from 1 in the membranes with DoG of 110 p.p., 49 p.p., 31 p.p. and 13 p.p. In Fig. 11b, the 200-point profiles (here we show average profiles fitted by 11–19 degree polynomials for simplicity), normalized in length (by membrane thickness) and in DoG (by minimum value in each SR profile), evidence that the curves with higher errors are the profiles with higher SR ranges and more abrupt variations, as expected.

For the estimation of the limit of detection (LOD) and the limit of quantification (LOQ), the standard deviation of the measurement points along the SR profiles (σ_{SR}) was obtained from the 200-point profiles. The root mean squared error (RMSE) of the polynomial fits to the raw profiles (Fig. 11b, before normalization) was taken as σ_{SR} . Values of $SR \pm 3\sigma$ and $SR \pm 10\sigma$ were plotted and linearly fitted for membranes with DoG ≤ 82 p.p., excluding the high-DoG outlier, yielding an excellent fit ($R^2 > 0.9999$) and indicating linear noise behavior with SR. LOD and LOQ were obtained by extrapolating the fits of $SR \pm 3\sigma$ and $SR \pm 10\sigma$ to the origin (Fig. 12, inset), resulting in LOD = 0.15 p.p. and LOQ = 0.57 p.p. For comparison, a conservative estimate based on the empirical σ_{SR} of the lowest-DoG membrane (DoG = 13 p.p., $\sigma_{SR} = 1.1 \times 10^{-2}$) gives LOD ≈ 0.74 p.p. and LOQ ≈ 2.5 p.p., consistent with the global RMSEP (≈ 3 p.p.). These two estimates illustrate the range between the theoretical limit derived from the heteroscedastic model and a conservative bound. All LOD and LOQ values are conditional on acquisition parameters (1 s per point, 50 $\times$ objective, 100% laser power) and can be improved by

longer acquisition or averaging.

Therefore, the integral-based model yields SR_{Tot} values that define a highly linear calibration curve (Fig. 9a). Combined with the low within-section standard deviation ($<2\%$), these results demonstrate the robustness and reliability of the method. The approach exhibits high sensitivity and precision across the full range of DoG values studied (13–110 p.p.), as evidenced by the excellent calibration linearity ($R^2 = 0.9981$) and the low dispersion between measurements, indicating that even small differences in local DoG can be reliably resolved. Accuracy and trueness are confirmed by comparison with gravimetrically measured overall DoG values, and selectivity is ensured by the method's ability to specifically resolve the grafted component without interference from the base polymer. For reference, a comparison with the simplified average SR across each section indicates that the resulting error would be around 3% for this dataset, suggesting that the method could be simplified in certain cases, albeit with slightly reduced accuracy. Taken together, these findings provide a solid basis for validation using the higher-resolution 200-point map (Fig. 13), which further allows an estimation of the detection capabilities, with LOD = 0.16 p.p. and LOQ = 0.57 p.p.

4.4. Parity plot and model validation

The predictive performance of the calibration model was tested using an independent validation set. In this case, the 200-point map was acquired from the same cross-section of the membrane as the calibration profiles. Although not fully independent, this more finely sampled dataset allows assessment of the model's ability to resolve local variations in DoG along the full gradient. A parity plot was used to compare the predicted DoG values (Fig. 13a), calculated from SRs, to the experimentally measured ones. The $y = x$ line was included as a reference for ideal correlation, with no fitting performed. The correlation with the $y = x$ line was strong, with a coefficient of determination (R^2) of 0.991. The root mean square error of prediction (RMSEP) was 2.86 p.p., and the bias was 0.62 p.p. These results indicate excellent predictive performance and support the physical model underlying the use of SRs. Absolute and percentage errors are shown in Fig. 13b and Fig. 13c, respectively. Given the physical expectation that the SR should be proportional to DoG, as discussed in Appendix A, a model constrained to pass through the origin was initially adopted as presented above. To assess potential systematic deviations, an alternative fit allowing a free intercept was also tested. This version slightly improved the statistical indicators ($R^2 = 0.996$, bias = -0.15 p.p., RMSEP = 1.96 p.p.) and removed the apparent trend observed in the residual error plot. Nevertheless, due to its stronger physical basis, the model without intercept was chosen for final calibration and discussion.

In addition to the predictive uncertainty of the calibration model, the repeatability of the reconstructed DoG profiles was assessed by comparing profiles obtained from independent cuts of membranes with low (13 p.p.), intermediate (51 p.p.), and high (110 p.p.) degrees of

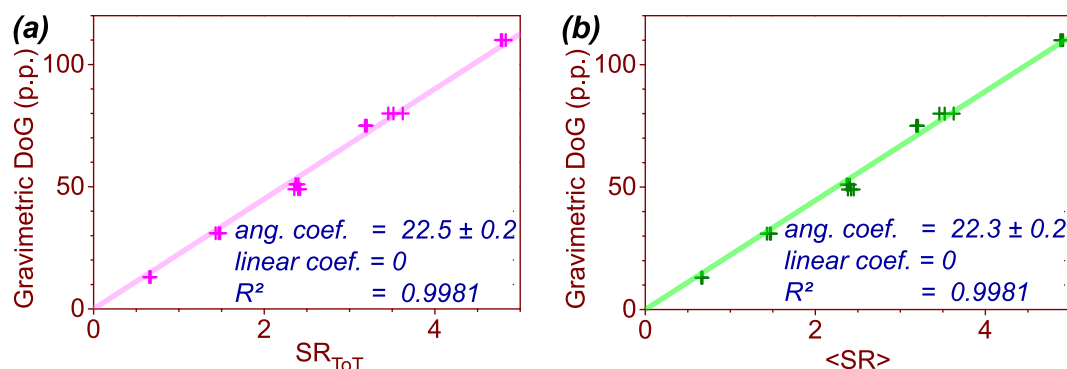


Fig. 9. Calibration curves. Calibration curve obtained with the SR_{Tot} (a) and with the average of the SRs along the membrane thickness (b).

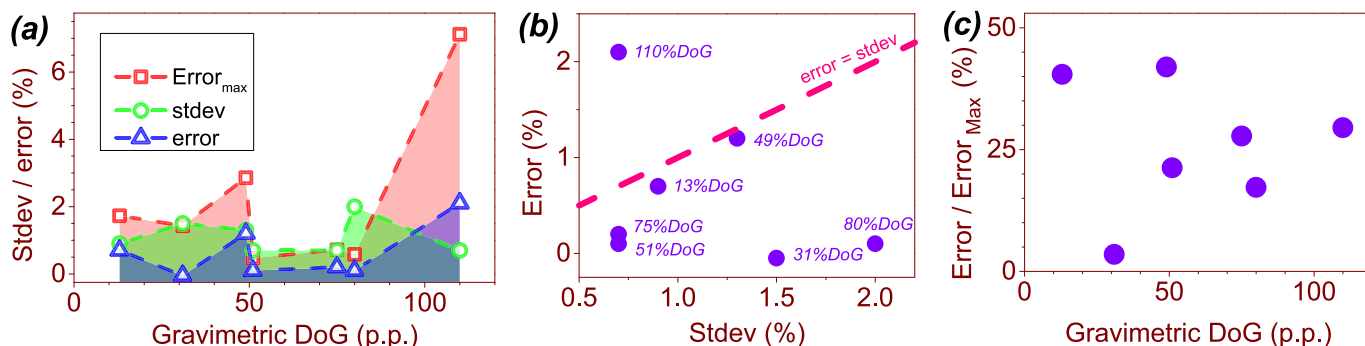


Fig. 10. Evaluation of errors in the average SR approach. Standard deviation between sample measurements, error between SR_{Tot} calculated with DoG-proportional swelling model and the average value along the membrane's SR profile and maximum error Error_{max} calculated with the bounding SRs and α .

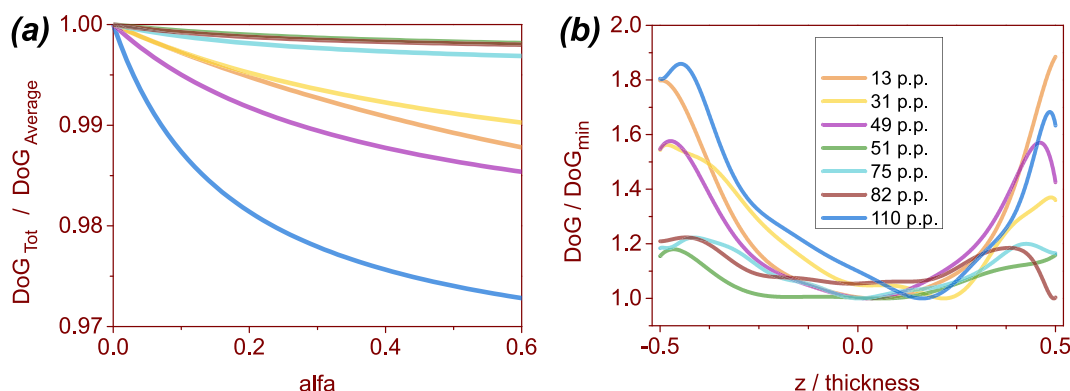


Fig. 11. (a) Variation of errors in the average SR approach. DoG total error in relation to the average DoG calculated for SR profiles shown in Fig. 8 and (b) fitted polynomials to the DoG profiles of Fig. 8, normalized in intensity to its minimum value and in z by the membrane thickness.

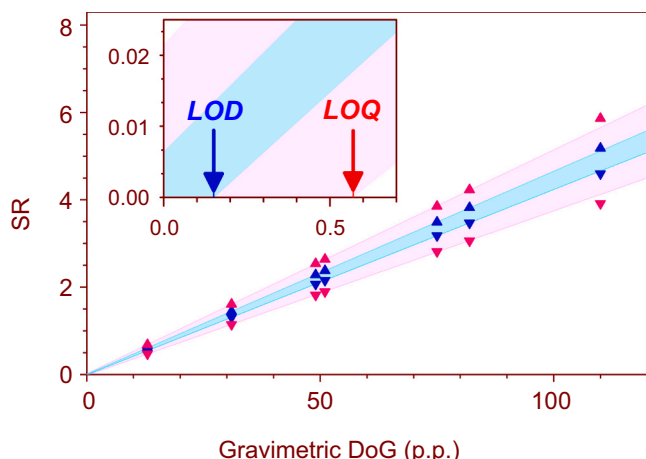


Fig. 12. Estimative of LOD and LOQ. SR ± 3σ (blue upwards and downwards triangle, respectively), SR ± 10σ (pink upwards and downwards triangle, respectively), with shaded bands defined by the linear fits to the SR ± 3σ and SR ± 10σ data (outlier at DoG = 110 p.p. was excluded). The inset shows a magnification of the low-DoG region, highlighting the corresponding LOD and LOQ positions.

grafting. As shown in Fig. S6, the majority of the profiles are highly reproducible and largely overlap for all three membranes. A deviation is observed for two profiles of the DoG = 51 p.p. membrane, which exhibit a deeper minimum at the membrane center compared to the remaining profiles. Given the total number of profiles analyzed (45 profiles across the three membranes), this behavior is attributed to local heterogeneity rather than a systematic effect. Importantly, this localized deviation

does not affect the overall trend of the DoG gradient nor the conclusions regarding graft distribution across the membrane thickness.

Fig. S6 shows overlapped profiles obtained from different cuts, together with the mean standard deviation calculated for each cut based on three measured profiles. When expressed in terms of DoG, the standard deviations obtained from individual profiles typically range from below 1 p.p. for low-DoG membranes to approximately 1–2 p.p. for intermediate and high-DoG samples, as shown in Fig. S7a. In this representation, the upper envelope of the standard deviation values exhibits an approximately linear trend with increasing DoG. These values are of the same order of magnitude, but generally smaller than the RMSEP obtained from the validation of the SR-to-DoG conversion. This indicates that the uncertainty associated with the calibration model does not dominate the observed spatial variability, allowing the reconstructed DoG profiles to be interpreted as physically meaningful within the experimental resolution of the method. Consistently, the corresponding envelope of the coefficient of variation (CV), shown in Fig. S7b, remains approximately constant across the investigated DoG range, with typical values around 2.5%. This indicates that the relative dispersion of the measurements is largely independent of DoG, supporting the robustness and repeatability of the reconstructed profiles.

We emphasize that the strong linearity observed between SR and DoG enables the use of SR profiles to estimate the overall DoG of membranes with unknown composition. However, the main goal here is not to determine the overall DoG, which is typically obtained through gravimetric analysis, but to resolve the local DoG distribution across the membrane thickness. Although the calibration curve in Fig. 9 could be applied to estimate the bulk DoG of unknown samples, the key contribution of this work lies in establishing a reliable proportional correlation between SR and DoG. Considering that this proportionality is accepted, any measured SR profile can be integrated using Eq. (6) to calculate

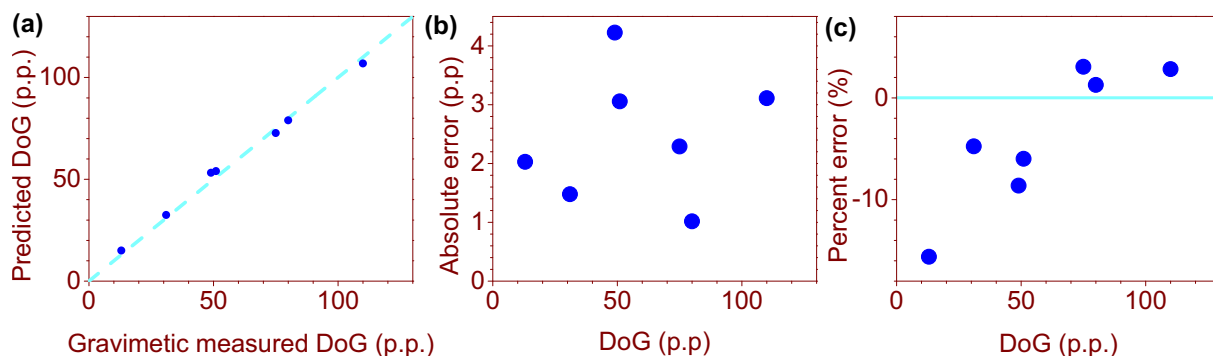


Fig. 13. Plots of the validation set of data. (a) Parity plot between the predicted and measured DoG, absolute (b) and percent(c) errors. Line in (a) represents $y = x$.

SR_{Tot} , which is then related to the gravimetrically measured overall DoG. This allows reconstruction of the local DoG profile using only a single reference measurement, eliminating the need for multiple standards or extensive calibration. In this case then the macroscopically measured $\tilde{\alpha}$ value may be a good approximation, since small sensitivity was observed.

4.5. Determination of the DoG profile of the asymmetric membrane

Finally, the technique was applied to measure the profile of an asymmetric ETFE-grafted membrane. Fig. 14a displays the measured SR profile (left axis) of the asymmetric membrane synthesized in the custom grafting reactor with two chambers containing VBC solutions at 60% and 10% (v/v). The SR profile was fitted with a 7th-degree polynomial. The polynomial degree was selected by incrementally increasing the order and visually evaluating the quality of the fit, until a satisfactory match between the curve and the data was achieved. The quality of the fit was confirmed by the homogeneous distribution of residuals along the membrane thickness, indicating the absence of systematic deviations (inset of Fig. 14a). Applying Eq. (6) to the fitted curve, a total SR of 3.21 was observed. As discussed above, in the absence of a model including a dependence of $\tilde{\alpha}$ on SR, a value of $\tilde{\alpha} = 0.36$ was used, corresponding to the average of the points above DoG 45 p.p. in Fig. 6d, since the measured DoG of the membrane was 70 p.p. Using the angular coefficient obtained from the calibration curve in Fig. 9, it was found a Raman-derived DoG of 72.2 p.p., with an estimated uncertainty of 2.9 p.p. (RMSEP). This value is only 2.2 p.p. (3.1%) higher than the gravimetrically measured value (70 p.p.) and the deviation remains within the RMSEP, indicating a good agreement between the Raman and gravimetrically measured DoG. The corresponding local DoG profile, calculated via this calibration, is shown on the right vertical axis of Fig. 14a, clearly revealing the expected gradient from left to right (from

~110 p.p. to ~40 p.p.).

The DoG profile obtained via calibration was then compared to a profile derived from the single membrane measurement, as shown in Fig. 14b. In both cases, the measured SR values were adjusted using a 7th-degree polynomial, and uncertainty was estimated by considering the RMSEP in the validation and the dispersion of the points in the polynomial adjustment (RMSE). The overlapping error bands in Fig. 14b confirm strong agreement between the two approaches.

It is worth emphasizing that both approaches shown in Fig. 14b lead to the determination of the same physical quantity, namely the local DoG, but rely on fundamentally different experimental strategies. The calibration-based approach requires the synthesis and characterization of multiple reference membranes, whereas the single-reference approach exploits the proportionality between SR and DoG, previously established through calibration and validation, and requires only one gravimetric DoG measurement of the membrane under study. It should be emphasized that the validity of the single-reference approach, in which a Raman SR profile is normalized using a single gravimetric DoG value, does not stem from the spectroscopic method itself but rather from the macroscopic homogeneity of the membrane under investigation, since the comparison with the gravimetric DoG takes into account a spatially averaged profile. Asymmetric membranes are inherently more heterogeneous than symmetric ones due to the absence of agitation and the spatially distinct grafting conditions during synthesis.

The reproducibility of the DoG profiles obtained for the asymmetric membrane was evaluated by comparing profiles measured from five independent cross-sections, with three profiles acquired per cut. As shown in Fig. S8, the reconstructed profiles are qualitatively similar and consistently exhibit the same asymmetric DoG gradient across the membrane thickness. Moderate differences in absolute SR and SR_{Tot} values are observed between cuts, reflecting the intrinsic heterogeneity of asymmetric membranes synthesized under non-agitated and spatially

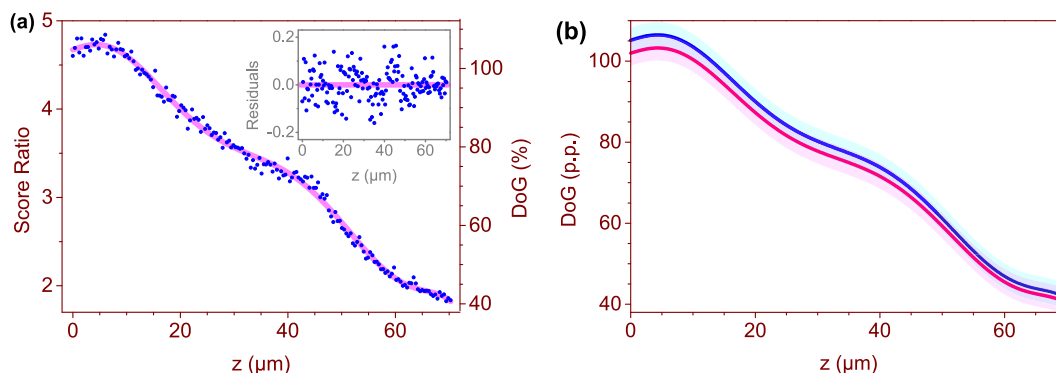


Fig. 14. SR profile measured for an asymmetric membrane synthesized with 60% and 10% VBC solutions on each side. Dots represent experimental data, and the magenta line corresponds to a 7th-degree polynomial fit. The inset shows the fit residuals. (b) DoG profiles (fitted polynomials) and associated error bands obtained using a single profile (pink) and the full set of calibration samples (blue).

asymmetric grafting conditions. For each cut, the experimental variability was estimated from the standard deviation of the three profiles. For the profile originally reported in Fig. 14, which corresponds to a single measurement, no experimental standard deviation can be assigned; instead, the uncertainty associated with the SR-to-DoG conversion (RMSEP) is indicated separately to enable comparison with the variability observed among independent cuts. Within these combined experimental and calibration uncertainties, the previously reported profile is consistent with the additional measurements and is representative of the asymmetric membrane.

Although the RMSEP obtained from the calibration represents the intrinsic uncertainty of the model, the dispersion observed among the SR_{Tot} values of the asymmetric membrane is of the same order or larger than this value. Therefore, the effective uncertainty associated with the estimated DoG_{Tot} is dominated by spatial variability within the membrane rather than by the calibration error itself. For this reason, the RMSEP should be regarded as a lower bound for the overall uncertainty, while the actual error increases as the homogeneity of the membrane decreases. This additional uncertainty does not arise from limitations of the spectroscopic method, but rather from structural heterogeneities inherent to the membrane fabrication process.

Importantly, the method based on a single SR profile combined with a gravimetric DoG measurement demonstrates high accuracy when sufficient macroscopic homogeneity is present and can be performed rapidly, requiring only minimal experimental effort, thereby highlighting its value for practical and high-throughput characterization of functional membranes. The approach is experimentally reproducible and applicable to asymmetric grafted membranes or similar polymer systems, provided that the underlying homogeneity assumptions are satisfied, and is consistent with established principles of analytical method validation.

5. Conclusions

We demonstrated, for the first time, the use of multivariate analysis to assess the DoG with spatial resolution in anion exchange membranes.

The score ratio between VBC and ETFE scores was shown to be proportional to the volume concentration of grafted chains, which implies that, for a uniform sample, the DoG is proportional to the score ratio.

A calibration curve can be obtained from a set of homogeneous samples. In the absence of such samples, the correlation between local and global score ratios is not expected to be straightforward, especially due to the intrinsic membrane swelling as it incorporates grafted side chains, making it difficult to infer overall grafting from local volumetric concentration measurements. The overall grafting was numerically estimated from a model that assumes local expansion is proportional to the local DoG, and the results were compared with gravimetric measurements, which serve as the established reference method for validation. The maximum errors generated in comparison with the simple average were estimated and found to be dependent on the SR ranges and smoothness of transition between high to low SR regions. For the expansion coefficient obtained for ETFE the error was inferior to the standard deviation for most of the measured points. This suggests that the average could be used instead. However, the maximum expected errors must be carefully evaluated.

Although the objective was not to quantify the overall DoG, the use of multivariate analysis was shown to provide an excellent prediction, with a high correlation coefficient ($R^2 = 0.991$) and an RMSEP of 2.9 p.p., confirming the quantitative robustness of the method. The strong linear relationship between the DoG and the score ratio demonstrates that it is possible to determine the DoG profile without a full calibration set. If the overall DoG (obtained gravimetrically) is known, and the score ratio profile is measured, the DoG profile can be derived by normalizing the score ratio to the known overall DoG. This approach was validated by measuring an asymmetric membrane, yielding a deviation of only

3.1% when compared to the DoG profile obtained using the full calibration curve. The error bands of both profiles overlapped throughout the thickness, indicating consistency between the results. These findings demonstrate that the local DoG profile can be reliably extracted from a single Raman measurement, provided that the overall DoG is known, offering a fast, simple, and accurate method for spatially resolved quantification.

The process was found to be highly sensitive to data treatment, particularly with respect to baseline correction, spectral range selection, and the precise alignment of reference and measured spectra. In addition, the spectral range was restricted to ensure consistent baselines across the dataset. After careful preprocessing, residuals from the CLS analysis were dominated by noise, with minimal systematic features around the peaks, indicating that the spectral decomposition using the selected loadings provided an excellent fit to the measured data, with high reproducibility and absence of systematic bias.

Overall, the method demonstrates high selectivity, specifically resolving grafted chains without interference from the ETFE matrix, and high sensitivity, with very low detection and quantification limits (LOD = 0.16 p.p. and LOQ = 0.57 p.p., with a conservative estimate of LOD $\approx$ 0.74 p.p. and LOQ $\approx$ 2.5 p.p.). The working range spans local DoG values from approximately 12 to 162 p.p., while the overall DoG of the membranes was 13–110 p.p. with accuracy and trueness are confirmed by agreement with gravimetric DoG values. Precision is supported by the low RMSEP from validation and the intra-section repeatability of better than 2%. Reliability is further indicated by the robustness of the calibration and consistency across different profiles, although broader validation across multiple independent membrane samples was not performed in this study. The present results strongly support the reproducibility of the approach, and future work may extend this validation to a wider range of materials and preparation conditions.

Microstructural variations such as chain length or branching are expected to induce only subtle changes in Raman spectra, which are secondary compared to the dominant compositional contrast associated with DoG. Accordingly, in its current implementation, the method is primarily sensitive to compositional variations and local graft distribution, while microstructural effects are not independently resolved. Future studies employing dedicated calibration sets may extend the approach toward explicit microstructural characterization.

In summary, we demonstrated a technique capable of locally quantifying the DoG, addressing a significant gap in currently available methods. A key advantage is that it relies on standard Raman equipment available in many laboratories worldwide. The ability to resolve the local DoG is particularly relevant for the novel asymmetric and/or non-homogeneous grafted membranes. Moreover, this approach is applicable to any grafted copolymer system with side-chain functionalization. And its validation parameters indicate suitability for routine analytical use, broadening its potential impact beyond the specific membranes studied. These membranes are designed to improve water management in alkaline fuel cells, and the proposed technique could be a key enabling technology for the development of the next generation of anion exchange membranes.

CRedit authorship contribution statement

Allan Berezki: Conceptualization, Data curation, Validation, Formal analysis, Investigation, Methodology, Software, Writing – original draft preparation; **Andrey da Silva Barbosa:** Conceptualization, Investigation, Methodology, Writing – review and editing; **Niklaus Ursus Wetter:** Writing – review and editing; **Dario R. Dekel:** Conceptualization, Writing – review and editing; **Elisabete Inacio Santiago:** Funding acquisition, Project administration, Supervision, Writing – review and editing.

Declaration of generative AI and AI-assisted technologies in the writing process

During the preparation of this work, the authors used ChatGPT (OpenAI) to improve the clarity, style, and readability of the text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Funding

The authors acknowledge the support from FAPESP (grant no. 2017/11987-4, grant no. 2017/11937-4) and Shell and the strategic importance of the support provided by ANP (Brazil's National Oil, Natural Gas, and Biofuels Agency). D.R.D. work was funded by the European Union's Horizon 2024 research and innovation program under grant agreement 101192454. The authors thank the funding support of CNPq IBH2-MCTI No. 405793/2022-7, CNPq SisH2 No. 407967/2022-2, CNPQ No. 153771/2024-0, FAPESP by projects No. 2022/07786-9 (M-ERA.NET), 2023/14931-4, 2024/12122-8, 2024/02220-2 and 2024/01763-2.

Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank the support given by the Radiation Technology Center at IPEN/CNEN for providing the facilities for the conduction of the experiments and data analysis. The Xplora-plus was financially supported by Financiadora de Estudos e Projetos (FINEP) grant 01.18.0073.00 and Instituto de Pesquisas Energéticas e Nucleares (IPEN) Edital Intercentros Announcement – Grant:2020 06.35. The authors acknowledge CECON (Centro de Combustível Nuclear) and CETER (Centro de Tecnologia das Radiações) for access to the FTIR Bruker INVENIO S equipment, which was acquired through the IAEA Project TC BRA 2019. The Article Processing Charge (APC) for this publication was funded by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – CAPES (ROR identifier: 00x0ma614). For the purpose of open access, the authors have applied a Creative Commons Attribution (CC BY) license to any Author Accepted Manuscript version arising from this submission.

Appendix A. Scores and DoG relation

In this appendix, we investigate the expected relationship between the CLS scores and the DoG.

In MRS, the spatial resolution is fundamentally limited by diffraction. Both the lateral (focal spot size w) and axial (depth of focus z_R) dimensions of the probing volume are determined by the excitation wavelength λ and the numerical aperture (N.A.) of the objective used in the MRS setup. This defines the effective sampling volume in which the Raman signal is collected and, consequently, the region over which the CLS scores are derived:

$$w = \frac{0.82 \cdot \lambda}{NA} \text{ and } z_R = \frac{\lambda \cdot n}{(NA)^2}, \quad (A.1)$$

where n is the refractive index of the medium. Typical values for w and z_R fall in the range of 500 nm to a few micrometers for high-NA objectives. For the conditions used in this work, (785 nm, N.A. = 0.5 and $n = 1.4$), the waist is 1.3 μm and the depth of focus is 4.4 μm . Given this scale, it is important to consider the internal structure of the grafted membranes, which is believed to consist of a heterogeneous mixture of crystalline and amorphous ETFE phases, along with grafted polymer domains. The characteristic dimensions of these microstructural features are on the order of ~ 10 nm [20], much smaller than the MRS probing volume. This implies that, during MRS acquisition, the MRS signal represents an averaged contribution from all these components simultaneously—crystalline, amorphous, and grafted polymer phases are illuminated and detected together.

When the laser beam is incident on the material, the Raman intensity $I(\tilde{\nu})$ emitted at a given Raman shift $\tilde{\nu}$ for a specific compound can be expressed as:

$$I(\tilde{\nu}) = P \cdot N \cdot \sigma(\tilde{\nu}), \quad (A.2)$$

where P is the power of the incident laser and $\sigma(\tilde{\nu})$ is the Raman emission cross section.

The number of scattering molecules in the laser interacting volume V is given by:

$$N = \rho \cdot V \cdot \frac{N_A}{M}, \quad (A.3)$$

where ρ is the mass density of the compound, M is the molar mass of the compound and N_A is the Avogadro number. For polymers, M corresponds to the molar mass of the repeating unit, as the Raman signal originates from these units and not from the full polymer chain.

$$I(\tilde{\nu}) = P \cdot \rho \cdot V \cdot \frac{N_A}{M} \cdot \sigma(\tilde{\nu}) \quad (A.4)$$

By considering the CLS method, the scores represent the relative contribution of each compound to the overall Raman spectrum of the sample. Therefore, for a given compound and Raman shift $\tilde{\nu}$, the score S is proportional to the corresponding Raman intensity:

$$S \propto I(\tilde{\nu}) \quad (A.5)$$

This expression shows that the Raman intensity is directly proportional to the mass density of the compound within the illuminated volume.

Substituting from Eq. (A.4):

$$S \propto P \cdot \rho \cdot V \cdot \frac{N_A}{M} \cdot \sigma(\tilde{\nu}) \quad (A.6)$$

By considering the two compounds, the base polymer (index B) and the graft chain (index G), the ratio between the scores SR is:

$$SR = \frac{S_G}{S_B} = \frac{P \cdot \rho_G \cdot V \cdot \frac{N_A}{M_G} \cdot \sigma_G(\bar{\nu})}{P \cdot \rho_B \cdot V \cdot \frac{N_A}{M_B} \cdot \sigma_B(\bar{\nu})} = \frac{\rho_G \cdot \frac{\sigma_G(\bar{\nu})}{M_G}}{\rho_B \cdot \frac{\sigma_B(\bar{\nu})}{M_B}} \quad (\text{A.7})$$

Since the Raman cross-sections $\sigma_G(\bar{\nu})$ and $\sigma_B(\bar{\nu})$, as well as the molar masses M_B and M_G , are constants, the ratio S_G/S_B can be directly related to the ratio of the mass densities of the grafted polymer and base polymer in the interaction volume.

An additional consideration is related to the nature of the Raman cross-section, which can be understood as a product of two factors: one related to the focusing geometry of the laser beam, and the other intrinsic to the material. However, given that both materials are homogeneously illuminated under the same optical conditions, and their characteristic domain sizes are much smaller than the laser spot, the focusing component is identical and cancels out in the SR. Therefore, only the intrinsic Raman cross-sections need to be considered in Eq. (A.7).

Since the same interaction volume is considered for both components, given that the laser interacts equally with all phases within its focal volume, the SR is also proportional to the ratio between the local masses of the graft and base polymer within that volume:

$$\frac{S_G}{S_B} \propto \frac{\rho_G}{\rho_B} = \frac{m_G^v}{m_B^v} \quad (\text{A.8})$$

The DoG, defined globally as the ratio between the grafted and original mass of the membrane, is given by:

$$DoG = \frac{m_f - m_i}{m_i} = \frac{m_G}{m_B}, \quad (\text{A.9})$$

where the masses are the total masses of the membrane. Considering the corresponding densities:

$$\rho_G = \frac{m_G}{V} \quad (\text{A.10})$$

$$\rho_B = \frac{m_B}{V} \quad (\text{A.11})$$

We arrive at the key result:

$$SR = \frac{S_G}{S_B} \propto \frac{\rho_G}{\rho_B} = \frac{m_G^v}{m_B^v} = \frac{m_G}{m_B} = DoG \quad (\text{A.12})$$

Therefore, even when considering the volumetric expansion of the membrane induced by grafting, the ratio of CLS scores between graft and base polymer remains proportional to the local DoG, provided the sample is homogeneous within the MRS interaction volume.

It is important to note that although grafting causes the membrane to swell, leading to a volumetric expansion of the material, the local densities of both the base polymer and the graft chains are reduced equally in a homogeneous sample. This means that the volumetric terms in Eq. (A.12) cancel out in the ratio, preserving the proportionality between the SR and the DoG. Therefore, the effect of expansion does not alter the SR in the case of a homogeneous membrane.

This result justifies the use of the normalized SR as a direct proxy for the local DoG in MRS-based mapping, as long as the sample can be considered locally homogeneous within the laser interaction volume.

Furthermore, by replacing Eq. (A.5) with an equivalent expression that considers either peak area or peak height instead of SRs, the rest of the derivation remains valid. In this case, the volumetric concentration of grafted chains, or, equivalently, the DoG in a homogeneous sample, can be expressed as being proportional to the ratio of peak areas or peak heights. These alternative metrics are therefore also suitable for determining the local DoG. However, precision tends to improve when moving from peak height to peak area and finally to CLS SRs, as each method progressively incorporates more spectral data. Additionally, when a broader spectral range is used, baseline variations tend to average out, resulting in greater consistency compared to single-peak analyses.

Appendix B. The DoG-proportional swelling model

In Appendix A, we have reference samples with a uniform DoG. However, for non-uniform samples, it is necessary to determine how to convert the local DoG(z) into a global DoG value that corresponds to the measured data. This conversion is essential because we measure a profile of SRs that is proportional to DoG, as previously demonstrated. It is important to note that the corrected global DoG should be equivalent to that of a uniform sample with the same overall DoG.

The global DoG, which is the gravimetrically measured value for the membrane, is given by:

$$DoG^{Tot} = \frac{M_f^{tot} - M_i^{tot}}{M_i^{tot}} = \frac{M_g^{tot}}{M_b^{tot}}, \quad (\text{B.1})$$

where:

- M_f^{tot} and M_i^{tot} are the total final and initial masses of the membrane, respectively.
- M_g^{tot} is the total mass of the grafted material.
- M_b^{tot} is the mass of the base polymer.

Since the grafting process induces volumetric expansion due to the incorporation of additional material, we initially assume an isotropic local expansion, where the volume increases proportionally to the local DoG:

$$\frac{dV'}{1 + \alpha \text{DoG}(z)} = dV \quad (\text{B.2})$$

where:

- dV' is the final volume after grafting and expansion.
- dV is the initial volume before expansion.
- α is the proportionality coefficient between volumetric expansion and DoG.

For a homogeneous sample, Eq. (B.1) can be rewritten as:

$$\text{DoG}_{\text{Tot}} = \frac{M_g^{\text{tot}}}{M_b^{\text{tot}}} = \frac{M_g^{\text{tot}} \cdot V'}{M_b^{\text{tot}} \cdot V} = \frac{\rho'_g}{\rho'_b}, \quad (\text{B.3})$$

where ρ'_g and ρ'_b represent the densities of the grafted material and the base polymer in the grafted sample, respectively. Considering that these densities can vary spatially (in this case, only along the z-axis), the local DoG is expressed as:

$$\text{DoG}(z) = \frac{\rho'_g(z)}{\rho'_b(z)} \quad (\text{B.4})$$

The densities are given by:

$$\rho'_b(z) = \frac{\rho_b^0}{1 + \alpha \text{DoG}(z)} \quad (\text{B.5})$$

$$\rho'_g(z) = \rho'_b(z) \cdot \text{DoG}(z), \quad (\text{B.6})$$

where ρ_b^0 is the initial density of the base polymer, defined as $\rho_b^0 = \frac{m_b}{V^0}$.

By integrating over the total volume, the total grafted mass is obtained as:

$$M_g^{\text{tot}} = \int_V \rho'_g(z) \cdot dV = \int_V \frac{\rho_b^0 \cdot \text{DoG}(z) \cdot dV}{1 + \alpha \text{DoG}(z)} \quad (\text{B.7})$$

Similarly, the total mass of the base polymer is given by:

$$M_b^{\text{tot}} = \int_V \rho'_b(z) \cdot dV = \int_V \frac{\rho_b^0 \cdot dV}{1 + \alpha \text{DoG}(z)} \quad (\text{B.8})$$

From these expressions, the global DoG can be determined:

$$\text{DoG}_{\text{Tot}} = \frac{M_g^{\text{tot}}}{M_b^{\text{tot}}} = \frac{\int_V \frac{\text{DoG}(z) \cdot dV}{1 + \alpha \text{DoG}(z)}}{\int_V \frac{dV}{1 + \alpha \text{DoG}(z)}} \quad (\text{B.9})$$

To estimate the coefficient α , we consider the total volume expansion:

$$dV^0 = \frac{dV'}{1 + \alpha \text{DoG}(z)} \quad (\text{B.10})$$

$$V^0 = \int_V \frac{dV}{1 + \alpha \text{DoG}(z)} \quad (\text{B.11})$$

By using Eq. (B.11) it is possible to numerically determine the expansion coefficient α by integrating the measured DoG profile in the grafted membrane and comparing with the original volume V^0 .

The volume integral has to be separated into an integral over the surface and another one along the membrane thickness. The expansion coefficient is also separated into two components in order to deal with different expansions along the thickness (α_t) and area of the membrane (α_s):

$$(1 + \alpha) = (1 + \alpha_t)(1 + \alpha_s) \quad (\text{B.12})$$

For a plane-parallel sample with a cylindrical volume element, the volume element can be written as:

$$dV = dA' dz \quad (\text{B.13})$$

By substituting in Eq. (B.11):

$$V^0 = \int_z \int_{A'} \frac{dA' dz}{1 + \alpha \text{DoG}(z)} = \int_z \frac{A' dz}{1 + \alpha \text{DoG}(z)} \xrightarrow{V^0} \frac{A^0 t^0}{A'} = \int_z \frac{dz}{1 + \alpha \text{DoG}(z)}, \quad (\text{B.14})$$

where A^0 is the initial cross-sectional area of the sample.

By using the same substitution, Eq. (B.9) can be written as an integral along z:

$$\text{DoG}_{\text{Tot}} = \frac{\int_0^t \frac{\text{DoG}(z) \cdot dz}{1 + \alpha \text{DoG}(z)}}{\int_0^t \frac{dz}{1 + \alpha \text{DoG}(z)}}, \quad (\text{B.15})$$

where t' is the final membrane thickness after grafting.

By inspecting Eq. (B.15), we note that for $\alpha = 0$ the expression reduces to the simple average taken along the membrane thickness. Another simple case we can consider is a uniform membrane with $\text{DoG}(z) = \text{DoG}_0$, where we obtain $\text{DoG}^{\text{Tot}} = \text{DoG}_0$.

By using the expressions Eqs. (B.14) and (B.15) were aimed to be used to compare the equivalent DoG, or the equivalent total SR, for the purpose of providing an equivalent total score ratio SR_{Tot} . In this case, the expansion coefficient α will be a different coefficient $\tilde{\alpha}$ relating the local expansion not proportional to the DoG but to the SR, supposing that the SR is proportional to DoG, then the expansion coefficient $\tilde{\alpha}$ will differ from the coefficient obtained for DoGs by a constant, but all the considerations remain the same. So, we can write:

$$\frac{t^0}{E_s} = \int_z \frac{dz}{1 + \tilde{\alpha}\text{SR}(z)} \quad (\text{B.16})$$

And

$$\text{SR}_{\text{Tot}} = \frac{\int_0^{t'} \frac{\text{SR}(z) \cdot dz}{1 + \tilde{\alpha}\text{SR}(z)}}{\int_0^{t'} \frac{dz}{1 + \tilde{\alpha}\text{SR}(z)}}, \quad (\text{B.17})$$

where $E_s = A'/A_0$ is the membrane surface expansion.

By using Eq. (B.16) it is possible to numerically calculate $\tilde{\alpha}$ by using the measured $\text{SR}(z)$ profiles and the measured surface expansion coefficient, and by using Eq. (B.17) it is possible to calculate the total score ratio in order to compare with the overall measured DoG on the membranes to provide a calibration curve.

Appendix C. Upper-bound error analysis for average-based DoG estimation

The expression for SR_{Tot} (Eq. (B.17)) can be interpreted as a weighted average of $\text{SR}(z)$, with weights $w = (1 + \tilde{\alpha}\text{SR}(z))^{-1}$. For $\tilde{\alpha} = 0$ Eq. (B.17) reduces to the continuous arithmetic mean of $\text{SR}(z)$ along the membrane thickness.

To gain insight into the behavior of Eq. (B.17), a simplified step-profile model is first considered, as shown in Fig. C.1a. In this case, SR_{Tot} becomes a weighted average between two SR values:

$$\text{SR}_{\text{Tot}} = \frac{aw_1(\tilde{\alpha})\text{SR}_1 + bw_2(\tilde{\alpha})\text{SR}_2}{aw_1(\tilde{\alpha}) + bw_2(\tilde{\alpha})}, \quad (\text{C.1})$$

where $aw_1 = a \cdot (1 + \tilde{\alpha}\text{SR}_1)^{-1}$ and $bw_2 = b \cdot (1 + \tilde{\alpha}\text{SR}_2)^{-1}$ are the weights for SR_1 and SR_2 , respectively.

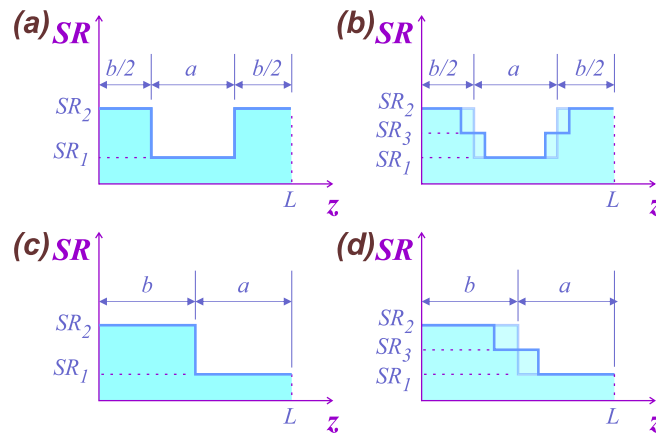


Fig. C.1. simplified symmetric (a) and asymmetric (c) step profiles and example of smoothed profiles obtained by adding intermediary steps (b) and (d).

The value SR_{Tot}^0 of the SR_{Tot} calculated for $\tilde{\alpha} = 0$ corresponds arithmetic mean weighted by the step lengths. As $\tilde{\alpha}$ increases, SR_{Tot} decreases and asymptotically approaches a limit $\text{SR}_{\text{Tot}}^\infty$, which is the weighted harmonic average:

$$\text{SR}_{\text{Tot}}^0 = \frac{a\text{SR}_1 + b\text{SR}_2}{a + b} \text{ and } \text{SR}_{\text{Tot}}^\infty = \frac{a + b}{a/\text{SR}_1 + b/\text{SR}_2} \quad (\text{C.2})$$

As an example of the behavior of SR_{Tot} as a function of $\tilde{\alpha}$, SR_{Tot} numeric values, normalized by the initial SR_{Tot}^0 of a membrane with a step rise SR profile were plotted as a function of $\tilde{\alpha}$ in Fig. C.2. In this example, a step profile with $a = 60 \mu\text{m}$, $b = 40 \mu\text{m}$ and SR of 1 and 0.5, respectively, was considered. The $\text{SR}_{\text{Tot}}/\text{SR}_{\text{Tot}}^0$ ratio decays quickly for small values of $\tilde{\alpha}$ and converges to ≈ 0.893 in this case.

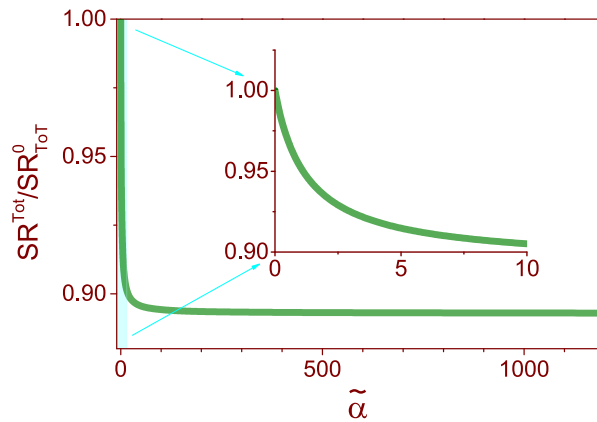


Fig. C.2. Ratio between SR_{Tot} and the average SR_{Tot}^0 as a function of the expansion coefficient $\tilde{\alpha}$ calculated for a membrane with $a = 60 \mu m$, $b = 40 \mu m$, $SR_1 = 1$ and $SR_2 = 0.5$. Insets show magnified scale for small values of $\tilde{\alpha}$ and the SR profile considered.

These results for SR_{Tot}^0 and SR_{Tot}^∞ can be extended to a profile with n SR steps because Eq. (C.1) generalizes accordingly, and SR_{Tot}^0 still represents the length-weighted arithmetic mean, while the limit SR_{Tot}^∞ corresponds to the length-weighted harmonic mean. Therefore, the **maximum error** introduced by using the arithmetic average instead of the $\tilde{\alpha}$ -dependent weighted result is given by the difference between SR_{Tot}^0 and SR_{Tot}^∞ .

To investigate how this maximum error behaves, the ratio between SR_{Tot}^∞ and SR_{Tot}^0 was calculated for different ratios $r = SR_2 / SR_1$ and fractional lengths $F = a / (a + b)$. Letting $a = F \cdot l$, $b = (1 - F) \cdot l$, and $a + b = l$, we obtain:

$$\frac{SR_{Tot}^\infty}{SR_{Tot}^0} = \left\{ \left[F + \frac{(1-F)}{r} \right] \cdot [F + (1-F) \cdot r] \right\}^{-1} \quad (C.3)$$

As shown in Fig. C.3a, this ratio is symmetric with respect to F , reflecting the symmetry between a and b . It reaches a minimum at $F = 0.5$, and decreases with increasing r . Five curves were plotted for $r = 1$ to $r = 3$. Only values for $r > 1$ are shown, since the result is symmetric with respect to $r \leftrightarrow 1/r$ (e.g., $r = 2$ yields the same curve as $r = 0.5$). In Fig. C.1b, curves are plotted for F in the range 0–0.5 and increasing r , showing the ratio between SR_{Tot}^0 and SR_{Tot}^∞ with increasing r . Only curves for F in the range 0–0.5 were plotted because curves for $F > 0.5$ overlap due to the symmetry in F . For $r = 1$, or $F = 0$ or $F = 1$, the SR profile is constant and both arithmetic and harmonic means are equal.

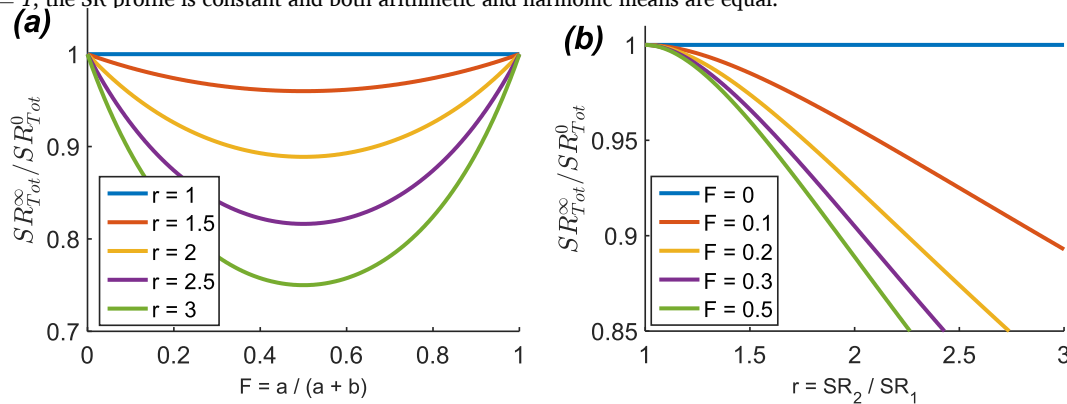


Fig. C.3. Ratio between the asymptotic value of $SR_{Tot}(\tilde{\alpha})$ and the average SR (obtained when $\tilde{\alpha}=0$) calculated for the step SR profile of Fig. C.1a (a) – as a function of F , calculated for different values of $r = SR_2 / SR_1$ and (b) – as a function of r calculated for different values of F .

From this, we conclude that the **maximum possible error** for a step profile is obtained for $F = 0.5$ and large r , corresponding to strongly asymmetric SR steps. Although this is a simplified case, the transition between SR_1 to SR_2 can be smoothed out, introducing intermediate steps e.g., (Figs. C.1b and C.1d) between SR_1 and SR_2 until it converges to a continuous profile. This will reduce the maximum error, since the harmonic mean increases with the addition of intermediate values (due to its sensitivity to low values), while the arithmetic mean remains unchanged. Because the terms in weighted average or in the weighted harmonic average can be swapped, this reasoning applies both to asymmetric profiles, (Fig. C.1c-d) as to symmetric profiles (Fig. C.1a-b), regardless of oscillations or monotonicity, because the order of the steps can be swapped to obtain a monotonic transition from SR_1 to SR_2 . Thus, the maximum error for a profile varying between SR_1 and SR_2 is bounded by the error in a step profile with $F = 0.5$, regardless of oscillations or monotonicity.

Finally, it is important to note that for most grafted membranes, the DoG, as well as the volume expansion, usually doesn't exceed 100% meaning the expansion factor α is usually below 1 (The value calculated by Eq. (B.2) for $V/V_0 = 2$ and $SR = 2$ is $\tilde{\alpha}=0.5$). This keeps the system far from the asymptotic limit and limits the error. However, the previous analysis still serves as a **worst-case estimate** for the error introduced by using the arithmetic average instead of solving Eq. 4, as well as to identify the behavior of the error, with the worst error calculated with $F = 0.5$. The maximum error at a given $\tilde{\alpha}$ can be estimated as:

$$Error_{max} = \frac{SR_{Tot}^0}{SR_{Tot}^{\tilde{\alpha}}} - 1 \quad (C.4)$$

Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2026.127558>.

Data availability

Data will be made available on request.

References

- [1] D.R. Dekel, Alkaline membrane fuel cell (AMFC) materials and system improvement - state-of-the-art, *ECS Trans.* 50 (2013) 2051–2052, <https://doi.org/10.1149/05002.2051ecst>.
- [2] M. Muhyuddin, C. Santoro, L. Osmieri, V.C.A. Ficca, A. Friedman, K. Yassin, G. Pagot, E. Negro, A. Konovalova, G. Lindquist, L. Twight, M. Kwak, E. Berretti, V. Di Noto, F. Jaouen, L. Elbaz, D.R. Dekel, P. Mustarelli, S.W. Boettcher, A. Lavacchi, P. Atanassov, Anion-exchange-membrane electrolysis with alkali-free water feed, *Chem. Rev.* 125 (2025) 6906–6976, <https://doi.org/10.1021/acs.chemrev.4c00466>.
- [3] M. Faour, K. Yassin, D.R. Dekel, Anion-exchange membrane oxygen separator, *ACS Org. Inorg. Au* 4 (2024) 498–503, <https://doi.org/10.1021/acscorginorgau.4c00052>.
- [4] S. Gottesfeld, D.R. Dekel, M. Page, C. Bae, Y. Yan, P. Zelenay, Y.S. Kim, Anion exchange membrane fuel cells: current status and remaining challenges, *J. Power Sources* 375 (2018) 170–184, <https://doi.org/10.1016/j.jpowsour.2017.08.010>.
- [5] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A. R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, *Energy Environ. Sci.* 7 (2014) 3135–3191, <https://doi.org/10.1039/c4ee01303d>.
- [6] L. Wang, J.J. Brink, J.R. Varcoe, The first anion-exchange membrane fuel cell to exceed 1 W cm^{−2} at 70 °C with a non-Pt-group (O 2) cathode, *Chem. Commun.* 53 (2017) 11771–11773, <https://doi.org/10.1039/C7CC06392J>.
- [7] A.L.G. Biancolli, D. Herranz, L. Wang, G. Stehlíková, R. Bance-Soualhi, J. Ponce-González, P. Ocón, E.A. Ticianelli, D.K. Wheligan, J.R. Varcoe, E.I. Santiago, ETFE-based anion-exchange membrane ionomer powders for alkaline membrane fuel cells: a first performance comparison of head-group chemistry, *J. Mater. Chem. A* 6 (2018) 24330–24341, <https://doi.org/10.1039/c8ta08309f>.
- [8] M. Mamlouk, J.A. Horsfall, C. Williams, K. Scott, Radiation grafted membranes for superior anion exchange polymer membrane fuel cells performance, *Int. J. Hydrog. Energy* 37 (2012) 11912–11920, <https://doi.org/10.1016/j.ijhydene.2012.05.117>.
- [9] C.E. Diesendruck, D.R. Dekel, Water – a key parameter in the stability of anion exchange membrane fuel cells, *Curr. Opin. Electrochem.* 9 (2018) 173–178, <https://doi.org/10.1016/j.coelec.2018.03.019>.
- [10] J. Xue, J.C. Douglin, K. Yassin, T. Huang, H. Jiang, J. Zhang, Y. Yin, D.R. Dekel, M. D. Guiver, High-temperature anion-exchange membrane fuel cells with balanced water management and enhanced stability, *Joule* 8 (2024) 1457–1477, <https://doi.org/10.1016/j.joule.2024.02.011>.
- [11] A.L.G. Biancolli, B.P. Silva Santos, E.I. Santiago, Radiation-grafted and cross-linked polymers-based anion exchange membranes, in: *Alkaline Anion Exch. Membr. Fuel Cells*, Wiley, 2024, pp. 211–240, <https://doi.org/10.1002/9783527837588.ch10>.
- [12] S. Mitov, G. Hübner, H. Brack, G.G. Scherer, E. Roduner, In situ electron spin resonance study of styrene grafting of electron irradiated fluoropolymer films for fuel cell membranes, *J. Polym. Sci. Part B Polym. Phys.* 44 (2006) 3323–3336, <https://doi.org/10.1002/polb.20982>.
- [13] M. Omichi, H. Hoshina, H. Morishima, K. Ohshima, N. Seko, Accurate measurement of the localized degree of grafting using thermogravimetric analysis, *Polym. Degrad. Stab.* 231 (2025) 111087, <https://doi.org/10.1016/j.polymdegradstab.2024.111087>.
- [14] B. Deng, J.Y. Li, Z. Hou, S. Yao, L. Shi, G. Liang, K. Sheng, Microfiltration membranes prepared from polyethersulfone powder grafted with acrylic acid by simultaneous irradiation and their pH dependence, *Radiat. Phys. Chem.* 77 (2008) 898–906, <https://doi.org/10.1016/j.radphyschem.2008.02.008>.
- [15] W. Geng, T. Nakajima, H. Takanashi, A. Ohki, Determination of total fluorine in coal by use of oxygen flask combustion method with catalyst, *Fuel* 86 (2007) 715–721, <https://doi.org/10.1016/j.fuel.2006.08.025>.
- [16] F. Wallasch, M. Abele, L. Gubler, A. Wokaun, K. Müller, G.G. Scherer, Characterization of radiation-grafted polymer films using CP/MAS NMR spectroscopy and confocal Raman microscopy, *J. Appl. Polym. Sci.* 125 (2012) 3500–3508, <https://doi.org/10.1002/app.36675>.
- [17] L. Gubler, M. Slaski, F. Wallasch, A. Wokaun, G.G. Scherer, Radiation grafted fuel cell membranes based on co-grafting of α -methylstyrene and methacrylonitrile into a fluoropolymer base film, *J. Membr. Sci.* 339 (2009) 68–77, <https://doi.org/10.1016/j.memsci.2009.04.031>.
- [18] W.H. Lee, C. Crean, J.R. Varcoe, R. Bance-Soualhi, A Raman spectro-microscopic investigation of ETFE-based radiation-grafted anion-exchange membranes, *RSC Adv.* 7 (2017) 47726–47737, <https://doi.org/10.1039/c7ra09650j>.
- [19] A.S. Barbosa, A.L.G. Biancolli, A.J.C. Lanfredi, O. Rodrigues, F.C. Fonseca, E. I. Santiago, Enhancing the durability and performance of radiation-induced grafted low-density polyethylene-based anion-exchange membranes by controlling irradiation conditions, *J. Membr. Sci.* 659 (2022) 120804, <https://doi.org/10.1016/j.memsci.2022.120804>.
- [20] A.L.G. Biancolli, A.S. Barbosa, Y. Kodama, R.R. de Sousa, A.J.C. Lanfredi, F. C. Fonseca, J.F.Q. Rey, E.I. Santiago, Unveiling the influence of radiation-induced grafting methods on the properties of polyethylene-based anion-exchange membranes for alkaline fuel cells, *J. Power Sources* 512 (2021) 230484, <https://doi.org/10.1016/j.jpowsour.2021.230484>.
- [21] T. Böhm, R. Moroni, M. Breitwieser, S. Thiele, S. Vierrath, Spatially resolved quantification of ionomer degradation in fuel cells by confocal Raman microscopy, *J. Electrochem. Soc.* 166 (2019) F3044–F3051, <https://doi.org/10.1149/2.0051907jes>.
- [22] F. Cardona, G.A. George, D.J.T. Hill, F. Rasoul, J. Maeji, Copolymers obtained by the radiation-induced grafting of styrene onto poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) substrates. 1. Preparation and structural investigation, *Macromolecules* 35 (2002) 355–364, <https://doi.org/10.1021/ma0022295>.
- [23] F. Cardona, G.A. George, D.J.T. Hill, S. Perera, Spectroscopic study of the penetration depth of grafted polystyrene onto poly(tetrafluoroethylene-co-perfluoropropylvinylether) substrates. 1. Effect of grafting conditions, *J. Polym. Sci. Part A, Polym. Chem.* 40 (2002) 3191–3199, <https://doi.org/10.1002/pola.10409>.
- [24] B. Mattsson, H. Ericson, L.M. Torell, F. Sundholm, Micro-Raman investigations of PVDF-based proton-conducting membranes, *J. Polym. Sci. Part A - Polym. Chem.* 37 (1999) 15–21, [https://doi.org/10.1002/\(SICI\)1099-0518\(19990815\)37:16<3317::AID-POLA30>3.0.CO;2-%23](https://doi.org/10.1002/(SICI)1099-0518(19990815)37:16<3317::AID-POLA30>3.0.CO;2-%23).
- [25] R.N. Samajdar, J. Goh, G.T. Smith, A.J. Wain, Raman spectroscopy for diagnostic analysis of fuel cell catalyst coated membranes, *Johnson Matthey, Technol. Rev.* (2024) 146–154, <https://doi.org/10.1595/205651325x17187054425007>.
- [26] P. Scharfer, W. Schabel, M. Kind, Mass transport measurements in membranes by means of in situ Raman spectroscopy—first results of methanol and water profiles in fuel cell membranes, *J. Membr. Sci.* 303 (2007) 37–42, <https://doi.org/10.1016/j.memsci.2007.06.051>.
- [27] P. Scharfer, W. Schabel, M. Kind, Modelling of alcohol and water diffusion in fuel cell membranes—experimental validation by means of in situ Raman spectroscopy, *Chem. Eng. Sci.* 63 (2008) 4676–4684, <https://doi.org/10.1016/j.ces.2008.03.014>.
- [28] S.W. Wakolo, K. Miyatake, J. Inukai, Transient distribution of water in an anion exchange membrane fuel cell monitored by operando coherent anti-stokes Raman scattering spectroscopy, *Electrochemistry* 92 (2024) 21–23, <https://doi.org/10.5796/electrochemistry.23-00140>.
- [29] S.W. Wakolo, D.A. Tryk, H. Nishiyama, K. Miyatake, A. Iiyama, J. Inukai, Various states of water species in an anion exchange membrane characterized by Raman spectroscopy under controlled temperature and humidity, *Phys. Chem. Chem. Phys.* 26 (2024) 1658–1670, <https://doi.org/10.1039/D3CP03660J>.
- [30] S.W. Wakolo, A. Syouji, M. Sakai, H. Nishiyama, J. Inukai, Coherent anti-stokes Raman scattering spectroscopy system for observation of water molecules in anion exchange membrane, *Spectrochim. Acta - part A Mol. Biomol. Spectrosc.* 309 (2024) 123875, <https://doi.org/10.1016/j.saa.2024.123875>.
- [31] N.A.F. Othman, S. Selambakkannu, T.A.T. Abdullah, Grafting yield determination of glycidyl methacrylate vapor on radiated kenaf fiber via FTIR spectroscopy, *Mater. Today Proc.* 29 (2019) 207–211, <https://doi.org/10.1016/j.matpr.2020.05.532>.
- [32] J.F. Madrid, M. Barsbay, L. Abad, O. Güven, Grafting of N,N-dimethylaminoethyl methacrylate from PE/PP nonwoven fabric via radiation-induced RAFT polymerization and quaternization of the grafts, *Radiat. Phys. Chem.* 124 (2016) 145–154, <https://doi.org/10.1016/j.radphyschem.2016.01.004>.
- [33] C. Schmidt, O. Töpfer, A. Langhoff, W. Oppermann, G. Schmidt-Naake, Depth profiling of graft polymer membranes via confocal laser scanning microscopy, *Chem. Mater.* 19 (2007) 4277–4282, <https://doi.org/10.1021/cm070174g>.
- [34] C. Schmidt, G. Schmidt-Naake, Grafting of 1-Vinylimidazole onto pre-irradiated ETFE films, *Macromol. Mater. Eng.* 292 (2007) 1067–1074, <https://doi.org/10.1002/mame.200700189>.
- [35] C. Schmidt, G. Schmidt-Naake, Proton conducting membranes obtained by doping radiation-grafted basic membrane matrices with phosphoric acid, *Macromol. Mater. Eng.* 292 (2007) 1164–1175, <https://doi.org/10.1002/mame.200700188>.
- [36] S.I. Sawada, Y. Maekawa, Radiation-induced asymmetric grafting of different monomers into base films to prepare novel bipolar membranes, *Molecules* 26 (2021), <https://doi.org/10.3390/molecules26072028>.
- [37] J. Shin, B.-S. Ko, S.-A. Kang, G. Fei, Y.-C. Nho, P.-H. Kang, A study on the distribution of polystyrene sulfonic acid grafts over the cross-section of a PFA film, *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms* 267 (2009) 791–794, <https://doi.org/10.1016/j.nimb.2008.12.009>.
- [38] L. Li, B. Deng, Y. Ji, Y. Yu, L. Xie, J. Li, X. Lu, A novel approach to prepare proton exchange membranes from fluoropolymer powder by pre-irradiation induced graft polymerization, *J. Membr. Sci.* 346 (2010) 113–120, <https://doi.org/10.1016/j.memsci.2009.09.027>.
- [39] A. Albert, A.O. Barnett, M.S. Thomassen, T.J. Schmidt, L. Gubler, Radiation-grafted polymer electrolyte membranes for water electrolysis cells: evaluation of key membrane properties, *ACS Appl. Mater. Interfaces* 7 (2015) 22203–22212, <https://doi.org/10.1021/acsami.5b04618>.
- [40] L. Wang, E. Magliocca, E.L. Cunningham, W.E. Mustain, S.D. Poynton, R. Escudero-Cid, M.M. Nasef, J. Ponce-González, R. Bance-Soualhi, R.C.T. Slade, D.

- K. Whelligan, J.R. Varcoe, An optimised synthesis of high performance radiation-grafted anion-exchange membranes, *Green Chem.* 19 (2017) 831–843, <https://doi.org/10.1039/C6GC02526A>.
- [41] V. Sproll, T.J. Schmidt, L. Gubler, Grafting design: a strategy to increase the performance of radiation-grafted membranes, *Polym. Int.* 65 (2016) 174–180, <https://doi.org/10.1002/pi.5041>.
- [42] B. Gupta, G.G. Scherer, Proton exchange membranes by radiation-induced graft copolymerization of monomers into Teflon-FEP films, *Chimia (Aarau)* 48 (1994) 127, <https://doi.org/10.2533/chimia.1994.127>.
- [43] T. Yamaki, K. Kobayashi, M. Asano, H. Kubota, M. Yoshida, Preparation of proton exchange membranes based on crosslinked polytetrafluoroethylene for fuel cell applications, *Polymer (Guildf)* 45 (2004) 6569–6573, <https://doi.org/10.1016/j.polymer.2004.07.048>.
- [44] C. Götz, M. Komma, D. Dworschak, S. Thiele, T. Böhm, Quantification of organic solvent concentration profiles in ion exchange membranes via confocal Raman microscopy, *Adv. Mater. Interfaces* 2300887 (2023) 1–12, <https://doi.org/10.1002/admi.202300887>.
- [45] C. Thibault, P. Huguet, P. Sizat, G. Pourcelly, Confocal Raman micro-spectroscopy and electrochemical investigation of anion transport through ion-exchange membranes, *Desalination* 149 (2002) 429–433, [https://doi.org/10.1016/S0011-9164\(02\)00770-1](https://doi.org/10.1016/S0011-9164(02)00770-1).
- [46] A.S. Barbosa, A.L.G. Biancolli, B.P.S. Santos, J.-J. Bonvent, D. Hermida-Merino, E. I. Santiago, Advancements in radiation-induced grafted anion-exchange membranes: controlling pre-irradiation parameters of high-density polyethylene for enhanced fuel cell performance and durability, *React. Funct. Polym.* 208 (2025) 106149, <https://doi.org/10.1016/j.reactfunctpolym.2025.106149>.
- [47] S. Deabate, P. Huguet, A. Morin, G. Gebel, Y. Lanteri, Z. Peng, A.K. Sutor, Raman microspectroscopy as a useful tool for in situ and operando studies of water transport in Perfluorosulfonic membranes for PEMFCs, *Fuel Cells* 14 (2014) 677–693, <https://doi.org/10.1002/fuce.201300236>.
- [48] H. Witjes, M. Van Den Brink, W.J. Melssen, L.M.C. Buydens, Automatic correction of peak shifts in Raman spectra before PLS regression, *Chemom. Intell. Lab. Syst.* 52 (2000) 105–116, [https://doi.org/10.1016/S0169-7439\(00\)00085-X](https://doi.org/10.1016/S0169-7439(00)00085-X).
- [49] T.P. Pandey, A.M. Maes, H.N. Sarode, B.D. Peters, S. Lavina, K. Vezzù, Y. Yang, S. D. Poynton, J.R. Varcoe, S. Seifert, M.W. Liberatore, V. Di Noto, A.M. Herring, Interplay between water uptake, ion interactions, and conductivity in an e-beam grafted poly(ethylene-co-tetrafluoroethylene) anion exchange membrane, *Phys. Chem. Chem. Phys.* 17 (2015) 4367–4378, <https://doi.org/10.1039/C4CP05755D>.
- [50] J. Qiu, M. Li, J. Ni, M. Zhai, J. Peng, L. Xu, H. Zhou, J. Li, G. Wei, Preparation of ETFE-based anion exchange membrane to reduce permeability of vanadium ions in vanadium redox battery, *J. Membr. Sci.* 297 (2007) 174–180, <https://doi.org/10.1016/j.memsci.2007.03.042>.
- [51] M. Mahmoud Nasef, H. Saidi, A. Ahmad, A. Ahmad Ali, Optimization and kinetics of phosphoric acid doping of poly(1-vinylimidazole)-graft-poly(ethylene-co-tetrafluoroethylene) proton conducting membrane precursors, *J. Membr. Sci.* 446 (2013) 422–432, <https://doi.org/10.1016/j.memsci.2013.05.053>.