Ionomer membranes are crucial components of many electrochemical devices. In this work, confocal Raman microscopy is employed to characterize Nafion ionomers quantitatively in pristine status and after usage as a proton exchange membrane in a fuel cell. Confocal Raman microscopy allows non-destructive thickness and equivalent weight measurements of Nafion with a 95% confidence interval of ±13 g mol⁻¹ at an equivalent weight of 1000 g mol⁻¹, which is significantly more accurate than previously reported methods. Characterization can be performed at a spatial resolution better than 2 μm, providing insights into local membrane degradation after fuel cell operation. Membrane thinning to less than 40% of the initial thickness of Nafion NR-211 occurs after a 100 h open circuit voltage hold, accompanied by an anisotropic increase of the equivalent weight from 1035 g mol⁻¹ to an average of 1200 g mol⁻¹. Most pronounced increases are found close to the anode. Further, the characterization of a Nafion XL membrane shows that its microporous reinforcement is represented as increased equivalent weight with local heterogeneities within the membrane. These results show that confocal Raman microscopy is a valuable tool to investigate ionomers that are used as ion exchange membranes in electrochemical devices.

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degradation to take place preferentially on the anode side\textsuperscript{16–18} or the cathode side\textsuperscript{15,19–21} of a MEA. Taking the contradictory results from literature into account, a strong influence of the operating conditions (e.g. cell voltage), the MEA components (e.g. Pt loading), and the overall cell design (e.g. material of flow fields) on membrane degradation can be expected. Thus, a reliable experimental approach for membrane characterization independent from cell design is required in order to elucidate chemical degradation modes.

Especially for chemically stabilized Nafion membranes with a reduced number of terminal $-\text{COOH}$ end groups,\textsuperscript{22} chemical degradation is supposed to occur via radicals attacking the sidechains of the PFSAs,\textsuperscript{10} which reduces the amount of $-\text{SO}_3^-$ groups in the polymer. The amount of $-\text{SO}_3^-$ groups in the polymer is typically quantified in gram of polymer per mole $-\text{SO}_3^-$ as the equivalent weight (EW). Thus, the EW is directly related to the stability and crystallinity of the ionomer as well as to its proton conductivity.\textsuperscript{23}

A variety of methods have been described that allow EW quantification of an ionomer. The standard method is titrimetry, which requires reliable drying and weight measurement as well as a titration step in order to calculate the EW.\textsuperscript{24} More sophisticated approaches such as elemental analysis, energy dispersive X-ray spectroscopy (EDX), or nuclear magnetic resonance spectroscopy have also been used.\textsuperscript{25} All of these methods can be applied to pure membranes, while reinforced membranes require approaches with spatial resolution. Moukheiber et al. showed that EDX-mapping is a suitable method for the analysis of these methods can be applied to pure membranes, while reinforced membranes require approaches with spatial resolution. Moukheiber et al. showed that EDX-mapping is a suitable method for the analysis of Nafion membranes and PTFE-reinforced Nafion XL membrane. To our knowledge, this is the first study to show that this approach is capable of reliable thickness and local EW measurements of ionomer membranes in the pristine state as well as after operation in a fuel cell, allowing determining loss of sidechains and membrane thinning quantitatively.

**Experimental**

**Nafion membranes and ionomer film preparation.**—Nafion dispersions DE2029, D2020 (Ion Power, USA), and D2021 (FuelCellStore, USA) were drop-cast on glass slides and solvents were allowed to evaporate at ambient air conditions. Aquivion D72-25BS (Sigma-Aldrich, USA) was prepared equally, however a thermal annealing step was performed in order to render the ionomer film water-insoluble. After drop-casting and solvent evaporation at room temperature, Aquivion D72-25BS was thermally annealed for 2 h at 180°C on a hotplate. Nafion membranes N117, NR-211, NR-212, and Nafion XL (Ion Power, USA) were investigated as received from the manufacturer.

The manufacturer provides an acid capacity range (ion exchange capacity: IEC) in meq g\textsuperscript{−1} of the ionomers which allows to calculate the EW in g mol\textsuperscript{−1} by 1000/IEC = EW. The EW of an ionomer is linked to the number of backbone repeat units per sidechain $m$ (compare Figure 1a) by $\text{EW} = m \cdot M_\text{SO}_3^{-} + M_\text{Me}^+$. Note that the backbone repeat unit that carries the sidechain is considered as being part of the sidechain in the conversion from EW to $m$. Thus, backbone and sidechain are labeled accordingly in Figure 1a. For Nafion and Aquivion the molecular mass of the backbone repeat unit $M_\text{Me}^+$ is 100 g mol\textsuperscript{−1}. The molecular mass of the sidechain $M_\text{SO}_3^-$ is 278 g mol\textsuperscript{−1} for Aquivion and 444 g mol\textsuperscript{−1} for Nafion.

**Fuel cell testing and accelerated membrane degradation.**—To shorten the time of ageing, four $1 \times 1$ cm\textsuperscript{2} MEAs were assembled in one cell fixture with a 25 cm\textsuperscript{2} serpentine flow field and operated in a Scribner 850e fuel cell test system. The cells were separated by PTFE-gaskets (240 $\mu$m thickness on each side) with cut-outs of 1.1 $\times$ 1.1 cm\textsuperscript{2} for each cell (see Figure S1). The MEAs were prepared with Nafion NR-211 membranes of $3 \times 3$ cm\textsuperscript{2} and gas diffusion electrodes of $1 \times 1$ cm\textsuperscript{2} with a Pt loading of 0.25 mg cm\textsuperscript{−2} (cathode) and 0.05 mg cm\textsuperscript{−2} (anode) on Freudenberg H245C (provided by Greenenergy, Germany). The cells were equilibrated over 1 h by 1 min voltage steps of open circuit voltage (OCV), 0.6 V, and 0.3 V; at full humidification, 80°C cell temperature, ambient pressure, and H\textsubscript{2}/O\textsubscript{2}. The accelerated stress test was conducted as OCV hold according to the department of energy (DOE) protocol.$^{24}$ H\textsubscript{2} crossover and electrical shorts were measured by linear sweep voltammetry (LSV) under H\textsubscript{2}/N\textsubscript{2}, fully humidified, ambient pressure, and 80°C (Figure S2a). The high frequency resistance (HFR) was measured by current interrupt at 3 kHz (Figure S2b). After 25 h, 50 h, and 75 h of OCV hold, one of the MEAs in the cell fixture was removed for Raman investigation after a total OCV hold time of 100 h.

**MEA preparation for Raman measurements.**—Carbon black at the electrodes is highly sensitive toward thermal degradation by laser irradiation and upon decomposition also destroys surrounding ionomer. Thus, all traces of electrode material needed to be removed prior to Raman measurements. A study that investigated ageing in Aquivion membranes by confocal Raman microscopy circumvented this problem by imaging cross sections of the MEA.\textsuperscript{33} However, using a single cross section of a MEA limits the accessible cell area to a single line. Further, preparing cross sections by physical sectioning e.g. with a razor blade might leave remnant carbon particles on the area to be investigated, which might impair subsequent Raman analyses. Therefore, we removed the electrodes of MEAs with a pulsed laser, which only ablates the electrodes without harming the membrane. A laser engraver (Trotec Speedy 300, Trotec, Austria) with a pulsed fiber laser (1064 nm) was used at 5 W, at a pulse frequency of 20 kHz, and at a speed of 0.2 m s\textsuperscript{−1} to remove electrodes. The membrane was fixed at the outer edges, with no physical contact to the device’s sample.
Stage below the laser target area. After 20 cycles of laser ablation on the active cell area, the electrodes were removed on both sides of the membrane without visual remnants being left.

In order to confirm that the laser ablation process did not alter the membrane, we compared the EW and thickness of a pristine NR-211 membrane with a Nafion NR-211 membrane that was part of a MEA and used within a break-in procedure. The latter is required to create a membrane with attached electrodes, as it is the case for MEAs after fuel cell operation. No significant differences were noticeable in the characteristics of pristine and electrode ablated membrane (Table S1).

Raman measurements.—When attempting a quantitative analysis of Raman spectra, it is important to keep the measurement conditions as constant as possible. For example, the sulfonyl group peak ν(S-O) is sensitive toward a change of the counter-ion. Another important factor for the intensity of this Raman band is the hydration status of the ionomer. A higher hydration level leads to a higher peak intensity and a slight red-shift of the ν(S-O) mode (Figure S3a). Thus, the quantitative analysis approach presented in this work can only be applied to ionomers at the same environmental conditions. According to Alberti et al., a more than 180 μm thick Nafion membrane (N117) already reaches a hydration level of more than 95% after immersion in water at room temperature for 1 h. Therefore, Raman measurements of ionomers were conducted after at least 1 h of immersion in DI water. Measurements were performed using a dedicated sample holder (Figure S3b and Figure S3c) for the analysis of hydrated samples and with a water immersion objective (Zeiss W Plan-Apochromat 63×/1.0). Additionally, the effect of membrane color changes needs to be taken into account. Nafion membranes turn from transparent to yellowish-brown upon long term storage. The color change is not a chemical reaction of the ionomer but rather occurs due to the uptake of organic compounds from the surrounding atmosphere. These compounds result in fluorescent background signals in Raman spectra and potentially interfere with the analysis of the spectra. It has been shown that prolonged irradiation of a sample with the Nafion excitation laser can effectively reduce background signals in samples exhibiting fluorescence (photo-bleaching). We adapted this process to our Raman measurements to eliminate possible skewing of Raman peak intensity ratios due to an underlying fluorescence signal. Background fluorescence was removed by photo-bleaching prior to Raman measurements with the same laser intensity as used for confocal Raman microscopy. Raman measurements were performed with a WITec alpha 300 RA (WITec, Germany) confocal Raman microscope. The microscope was equipped with a 532 nm laser that was used at a power of 50 mW. Spectra were acquired by a WITec UHTS 300 VIS-NIR spectrometer with a Peltier-cooled back-illuminated CCD-camera (1024 pixel) and a 1200 grooves mm⁻¹ optical grating. The system had a spectral resolution of approximately 2 cm⁻¹. Single spectra were acquired with an integration time of 5 s and by accumulating 5 spectra after 1 min of photo-bleaching. Depth scans through membranes were performed with equal settings, yet for reasons of time and sample stability without photo-bleaching prior to the acquisition of spectra. Omitting photo-bleaching did not affect EW trends over depth (see EW of NR-211 at beginning of test (BOT) in Figure 4c). Single spectra of the depth scans were acquired for 5 s and with 5 accumulations in 1 μm intervals through hydrated membranes. For the membrane degradation analysis, 10 depth scans at different locations per sample were performed.

The axial resolution of the setup was 1.6 μm (full width at half maximum intensity of the 520 cm⁻¹ peak profile of Si), determined by a confocal depth scan on a plain Si wafer. Since the refractive index of hydrated Nafion is almost identical to water (1.35 and 1.33), constant heat input to a sample by long measurement times potentially leads to thermal degradation and thereby might alter the ratio between peaks in the Raman spectrum. By performing a time-series
over 30 min of continuous Raman measurements at a single location on a Nafion membrane, we excluded that the ionomer was degraded by our measurement settings (Figure S5).

**Data processing.**—Removal of cosmic rays and background subtraction of the Raman spectra was performed using WITec Project FIVE+. Filter settings for cosmic ray removal in single spectra were chosen manually as required in order to remove artifacts. Datasets from confocal depth scans were automatically processed by a filter size of 4 and a dynamic factor of 5. Background subtraction was applied equally on all acquired data using the shape-based algorithm of the software with a shape size of 100 and a noise factor of 1.

MATLAB (MathWorks, USA) was used for all further processing steps. First, a calibration curve for Nafion was established using the commercially available dispersions Nafion DE2029, Nafion D2020, and Nafion D2021. The area under the curve of the four vibrational modes \(v_1(C-F)_{bb}\) (685 to 760 cm\(^{-1}\)), \(v_1(C-O-C)\) (770 to 831 cm\(^{-1}\)), \(v_1(C-O-C)\) (945 to 1001 cm\(^{-1}\)), and \(v_1(S-O)\) (1037 to 1081 cm\(^{-1}\)) was summarized. By plotting the ratios between the different sidechain-related peak intensities and the backbone-related peak intensity \(v_1(C-F)_{bb}\) over the inverse number of backbone repeat units per sulfonate group \((1/m, \text{as provided by the manufacturer of the Nafion dispersions})\), a linear correlation between Raman peak intensity ratio and ionomer EW was obtained (Figure 2) according to Equation 1. Five single measurements were acquired at different locations per ionomer sample and were used as input for a linear regression. Under the premise that pure PTFE does not show any of the sidechain-related peaks, linear fits were created after comparing the spectrum of the long side chain (LSC) ionomer Aquivion, Peng et al. attributed this peak to the stretching mode of the C-F bonds within the ionomer sidechain.\(^{41}\) A comparison of the spectra of LSC and SSC ionomers with a virtually identical ratio \(m\) between backbone repeat units and sidechains (Figure 1c) reveals a strong difference in the intensity of the peak at 804 cm\(^{-1}\). Since both SSC and LSC ionomer only contain one sulfonate group per sidechain, the intensity of this peak is expected to be approximately equal when contributing it to the \(v_1(C-O-C)\) mode. Nafion, however, has a longer sidechain and therefore harbors more C-F bonds per sidechain than Aquivion (Figure 1a). We therefore agree with the work by Peng et al. and suggest the assignment of the C-F stretch of the sidechain \(v_1(C-F)_{sc}\) to the peak at 804 cm\(^{-1}\).\(^{41}\) While the same vibrational mode of the ionomer backbone \(v_1(C-F)_{bb}\) is located at 732 cm\(^{-1}\).

**EW-Raman intensity calibration curve.**—Raman spectra are often analyzed only qualitatively since the absolute intensity of a sample not only depends on the sample, but, for example, also on the sensitivity of the spectrometer and on measurement settings like laser power and integration time. Therefore, a reliable normalization method is required to compare spectra quantitatively. Korzeniowski et al. established confocal Raman microscopy as a tool for quantifying the EW of bis-perfluorosulfonyl imide ionomers by normalizing spectra relative to their total spectral area.\(^{33}\) This normalization method is suitable for compensating spectral data of samples with different densities. However, it is a potential source of bias when analyzing ionomers with Raman spectra that are substantially different from the spectrum of the original polymer, because this normalization approach is performed under the assumption that the total spectral intensity of the ionomer remains constant when changing the ratio \(m\) of backbone repeat units per sidechain (Figure 1a). Thus, we used a quantification approach for the EW of Nafion that is independent from this normalization-related bias. As the EW of an ionomer is determined by the ratio between sidechains and backbone repeat units, one can focus on the ratio between two Raman peaks that are related to sidechain and backbone in order to calculate the EW without the need to normalize spectra. As the intensity of a Raman peak is directly dependent on the number of sampled molecules,\(^{46}\) the following correlation can be established:

\[
\frac{1}{m} = K \cdot n \cdot a_w \cdot I_{sc} = a_w \frac{I_{sc}}{I_{bb}} \Rightarrow a_w = \frac{I_{sc}}{I_{bb}} \cdot \frac{1}{a_w} \cdot m \quad [1]
\]

with the number of backbone repeat units per sidechain \(m\), Raman measurement constant \(K\) (e.g., excitation wavelength and laser power), the number of sampled molecules \(n\), and the Raman intensities of a sidechain-related peak \(I_{sc}\) and a backbone-related peak \(I_{bb}\). The two

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**Table I. slopes and coefficients of determination of the linear correlation between Raman intensity ratios and the ratio of sidechains per backbone repeat unit as displayed in Figure 2.**

|                | Linear correlation | Coefficient of determination |
|----------------|--------------------|-----------------------------|
| \(A = v_1(C-F)_{sc}\) | \(y = 1.7559 (1/m)\) | \(R^2 = 0.9837\) |
| \(A = v_1(C-O-C)\) | \(y = 1.0390 (1/m)\) | \(R^2 = 0.9805\) |
| \(A = v_1(S-O)\) | \(y = 2.0828 (1/m)\) | \(R^2 = 0.9920\) |

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**Figure 2.** Correlation between Raman spectrum and sidechain to backbone repeat unit ratio of Nafion dispersions. Shown are mean ratios of different Raman sidechain peaks to the \(v_1(C-F)_{bb}\) peak over the ratio of sidechains per backbone repeat unit of the Nafion dispersions DE2029 \((m = 4.34)\), D2020 \((m = 4.88)\), and D2021 \((m = 5.68)\). Horizontal error bars indicate the SD of the single Raman spectra that were acquired per sample.
factors $\alpha_{sc}$ and $\alpha_{bb}$ represent the specific Raman activities of the two investigated vibrational modes. All spectral information is obtained within one single measurement and therefore $n$ and $K$ are identical for both investigated peaks. The specific Raman activity of the peaks is unknown. Consequently, the factor $\alpha_{sc}/\alpha_{bb}$ must be determined experimentally for every pair of investigated sidechain- and backbone-peaks, leading to a simplified version of the equation with $a$ being the slope of a linear correlation. Equation 1 also holds true for PTFE with no sidechain-peaks (Figure S6a) and therefore meets the origin at infinite $m$. In order to establish this correlation as a calibration curve for Nafion, we measured different Nafion samples with known EW (DE2029, D2020, and D2021). Figure 2 shows the intensity ratio of several sidechain-related vibrational modes ($\nu_{s}(C-F)^{bb}$, $\nu_{s}(C-O-C)$, or $\nu_{s}(S-O)$) divided by the backbone-associated $\nu_{s}(C-F)^{bb}$ mode over the sidechain to backbone repeat unit ratio $1/m$. For all the investigated sidechain peaks, a linear correlation exists (Table I), with only the slope being different as expected.

Although displaying the ratio of Raman peaks directly over the EW of the ionomer seems more intuitive, there is no linear correlation between both, since the EW is not a ratio between sidechains and backbone repeat units, but a ratio between the total weight of the ionomer (sidechains and backbone) and the sidechains. Also, it is noteworthy that from the structure formula of the ionomer (Figure 1a) one would expect $1/(m+1)$ to be the correct estimate for the Raman peak intensity ratio in Equation 1, since basically one backbone repeat unit is considered as part of the ionomer sidechain. However, we found empirically that using $1/m$ instead of $1/(m+1)$ in Equation 1 results in a better linear correlation. This finding can be explained by a potential influence of the ether-bond that connects sidechain and backbone on the wavenumber of the $\nu_{s}(C-F)$ mode of directly adjacent C-F-bonds in the polymer main chain (Figure 1a). This hypothesis is consistent with the distinction between the vibrational modes $\nu_{s}(C-F)^{sc}$ and $\nu_{s}(C-F)^{bb}$, which is also based on a different Raman shift of the symmetric C-F stretch in the ionomer sidechain as compared to the same vibrational mode in the backbone.

The symmetric stretch mode of the sulfonyl group shows the highest intensity of all investigated sidechain-peaks (Figure 1) and consequently the impact of random spectral noise on the result is lowest when using this peak for the analysis. Also, the sulfonyl group is the best indicator for the EW of an ionomer when taking into account that partial degradation of sidechains might leave one or both of the ether-bonds in place but remove the sulfonyl group. Therefore, we used the calibration curve between the $\nu_{s}(S-O)$ mode and the $\nu_{s}(C-F)^{bb}$ mode for all further measurements. Note that all measurements were performed in the hydrated form of the ionomers in order to achieve equal intensities of the hydration-dependent $\nu_{s}(S-O)$ mode (compare Figure S3a).

| Sample      | EW, manufacturer  | EW ± SD, measured |
|-------------|--------------------|-------------------|
| Nafion N117 | 990–1053           | 1028 ± 6          |
| Nafion NR-211| 990–1053          | 1027 ± 3          |
| Nafion NR-212| 990–1053          | 1022 ± 6          |

The EW measurement of commercial Nafion membranes.—For Nafion N117, NR-211, and NR-212 the manufacturer states an EW range from 990 to 1053 g mol$^{-1}$. Using confocal Raman microscopy we obtained values between 1022 and 1028 g mol$^{-1}$ for the three membranes (Table II). According to the manufacturer only casting procedure (extrusion or dispersion-casting) and thickness of the membranes differ. Thus, a highly similar if not identical EW can be expected for the membranes as they are based on the same, chemically stabilized form of Nafion. While the EW of extruded Nafion N11x membranes is equal to the EW of dispersion-cast NR-21x membranes, the crystallinity of the two membrane types was reported to be different (see and sources therein). Raman spectroscopy is sensitive toward crystallinity changes in PTFE, and Gruger et al. suggested a change in the width of the $\nu_{s}(C-F)^{bb}$ mode according to the sample crystallinity. Despite these reports no observable differences exist in our data between extruded and dispersion-cast Nafion (Figure S6b). We therefore conclude that at least within the crystallinity range of commercially available Nafion membranes the differences are too small to have a significant impact on the investigated Raman peaks.

Moukheiber et al. published a comprehensive analysis of the accuracy of different chemical methods that are available for the determination of an ionomer’s EW. Methods such as titration, EDX, elemental analysis, and IR spectroscopy were used to determine the EW of various ionomers and the accuracy of the measurements was presented as a deviation from the values given by the manufacturer. These methods typically featured standard deviations (SD) from ±0.05 meq g$^{-1}$ (ion exchange capacity) up to ±0.08 meq g$^{-1}$. This corresponds roughly to ±50 g mol$^{-1}$ up to ±80 g mol$^{-1}$ for a Nafion membrane with an EW of 1000 g mol$^{-1}$. In contrast, the confocal Raman microscopy approach proved to be more accurate with a 95% confidence interval (±2 SD) of ±13 g mol$^{-1}$ for an EW = 1000 g mol$^{-1}$ Nafion sample according to our calibration curve (Figure 2).

Next, we applied our approach on the multi-layered membrane Nafion XL. Since it is not reasonable to determine the EW of this reinforced membrane based on single-spot measurements, as there are substantial differences between the outer Nafion layers and the inner PTFE-reinforcement, a confocal depth scan through the membrane was performed. Figure 3a depicts the calculated EW of Nafion XL over membrane thickness. The outer layers (pure Nafion with SiO$_2$ particles) of Nafion XL show a highly homogeneous EW of around 970 g mol$^{-1}$ while within the microporous PTFE reinforcement layer the EW is less homogeneous and reaches peaks of more than 2000 g mol$^{-1}$. A clear distinction between PTFE and Nafion within the reinforcement layer is not possible due to the resolution limits of confocal light microscopy. Thus, the EW trend of the depth scan creates the impression of local EW changes, which actually originate from local distribution differences between Nafion and PTFE-reinforcement that are beyond the spatial resolution of confocal light microscopy. Although Nafion that is present in the pores of the reinforcement layer is similar to the Nafion in the outer layers, the increasing ratio of PTFE to Nafion in the reinforcement layer results in very high EWs around 2000 g mol$^{-1}$. A virtual cross-section of Nafion XL is shown in Figure 3b, with the different chemical phases displayed in Figure 3c, which highlights the inhomogeneous reinforcement layer of the membrane. The EW results of Nafion XL are roughly consistent with the values provided by Moukheiber et al., who determined the EW of Nafion XL with EDX to approx. 910 g mol$^{-1}$ in the Nafion-rich outer layers and approx. 1790 g mol$^{-1}$ in the PTFE-rich central layer. A possible explanation for the lower EW in the outer layers of Nafion XL determined by Moukheiber et al. as compared to this work is the potential influence of the silica particles in Nafion XL on EDX-measurements, which may add additional oxygen-signals and therefore skew the result toward a higher sidechain-content.

Membrane degradation analysis.—Besides analyzing standard and reinforced membranes, confocal Raman microscopy can also be employed to investigate ionomer membranes after operation in a PEMFC. For this purpose, a Nafion NR-211 membrane was operated in accelerated stress test conditions according to DOE test for chemical membrane degradation (here: 100 h operation at OCV conditions). Within this timeframe, the cell voltage dropped remarkably from 0.94 V to 0.21 V, with a strong decrease in the first 10 h, followed by a plateau and another strong decrease after 75 h (Figure 4a). This trend including the spikes from interrupting the OCV hold is consistent with published data and most probably reflects membrane thinning and pinhole formation, leading to increased gas permeation and radical formation, which in turn attack the membrane polymer. $\text{H}_2$ crossover supports this interpretation, showing a more than
Figure 3. Characterization of Nafion XL with confocal Raman microscopy. 

(a) Single depth scan through Nafion XL. Raman spectra were taken at every 1 μm and the EW over depth is displayed. 

(b) Virtual cross-section through water-immersed Nafion XL with false-color display of the different phases in the membrane. 

(c) Raman spectra of the chemical phases in Nafion XL. The scan was performed with a 300 grooves mm$^{-1}$ optical grating, at an isotropic pixel size of 0.5 μm, and with an integration time of 0.5 s per pixel. Spectra are normalized to maximum peak intensity. Phase assignment in the Raman image was performed using a custom-built MATLAB code.

Figure 4. Membrane changes upon accelerated stress testing. 

(a) OCV over time. 

(b) Gas crossover and membrane thickness over time. 

(c) EW changes during OCV hold over membrane z-position. Lines correspond to mean of 10 measurements ±SD.

Table III. Fuel cell and membrane parameters measured prior and post accelerated stress testing. EW and membrane thickness are given as mean values ±SD of 10 individual measurements.

|                | Mean EW [g mol$^{-1}$] | Membrane thickness [μm] | H$_2$-crossover [mA cm$^{-2}$] |
|----------------|------------------------|--------------------------|-------------------------------|
| BOT            | 1035 ± 10              | 30.1 ± 0.3               | 4.35                          |
| 25 h OCV       | 1076 ± 30              | 28.8 ± 2.9               | 5.64                          |
| 50 h OCV       | 1107 ± 67              | 19.9 ± 2.6               | 6.29                          |
| 75 h OCV       | 1171 ± 101             | 16.6 ± 3.4               | 13.46                         |
| 100 h OCV      | 1200 ± 127             | 11.0 ± 3.1               | 68.43                         |

A tenfold increase from 4.35 mA cm$^{-2}$ at BOT to 68.43 mA cm$^{-2}$ after 100 h OCV hold, with a strong increase after 75 h (Figure 4b).

Using confocal Raman microscopy, we determined the thickness of the membranes after electrode removal. The thickness of the hydrated membrane decreased from 30.1 μm (BOT) to 11.0 μm after 100 h OCV (Figure 4b, Table III). Thickness discrepancy of NR-211 at BOT from the nominal value given by the manufacturer (25.4 μm) is attributed to membrane swelling, since measurements were performed in water immersion. Note that the reported thinning corresponds to the measured average thickness only. Thus, small deviations such as the formation of local pinholes were not taken into account. Between BOT and 75 h OCV, a correlation between membrane thinning and increasing H$_2$ crossover can be seen (Figure 4b), which can be explained by an increase in the gas diffusion rate with decreasing membrane thickness. The steep increase in H$_2$ crossover from 75 h to 100 h OCV hold most likely reflects the formation of pinholes in the membrane, which increase gas crossover substantially and independently from the measured thickness.

The EW of aged membranes was determined by applying the calibration curve obtained in Figure 2 on confocal depth scans of aged Nafion NR-211. With this approach the EW of the membranes was quantified locally between cathode and anode using the high spatial resolution of confocal light microscopy in the low single-digit micrometer range. We found that the EW increased gradually with longer OCV times, with only a minor effect on the cathode side and the highest increase between the anode and the center of the membrane (Figure 4c). Since Ghassemzadeh and Holdcroft found that for NR-211 chemical degradation occurs mainly via cleavage of sidechains, EW measurements are a valid indicator for membrane ageing. Our results support the theory of Liu and Zuckerbrod, who found a higher concentration of H$_2$O$_2$ at the anode side of a PEMFC, which may lead to a
preferred radical formation at the catalyst layer of the anode side and subsequently lead to an anisotropically accelerated membrane degradation at the anode of the fuel cell. Similar results have been reported by Zatoń et al., who performed Raman spectroscopy on Nafion membranes of aged MEAs and found that sidechain-related peaks were lost mostly on the anode side. Furthermore, in our data we see the most pronounced increase in the EW not directly at the anode side, but between the anode and the center of the membrane. Based on our results, we hypothesize for the entire process of membrane thinning that membrane degradation initially increases the EW by the loss of sidechains. This might be followed by break-down of the PTFE-backbone, which is reflected in the decrease of the EW toward the anode (Figure 4c). Finally, the ionomer is completely lost, which reduces overall membrane thickness.

Besides an anisotropic ageing between anode and cathode our data also shows that degradation proceeds inhomogeneously over the xy-plane of the membrane. As it can be seen in Figure 4c and Table III, the SD of the single EW measurements increased with longer OCV hold, meaning that local discrepancies in the EW of the membrane became larger with more elevated degradation status. Inhomogeneous membrane ageing is consistent with the work of Shi and Baker, who analyzed the spatial distribution of signs of chemical degradation in a Nafion NR-212 membrane. An OCV hold as an accelerated stress test shows rapid membrane degradation, but the underlying ageing does not necessarily display the same progression as in fuel cells operated at normal working conditions. Also, changes in fuel cell design such as electrode morphology and catalyst loading may influence ageing mechanisms. Thus, different cell types and working conditions are a plausible explanation for the contradictory results found in literature that suggest membrane degradation to take place preferentially on the anode side\(^{16,17}\) or the cathode side\(^{15,19-21}\) of a MEA. Further, Chandersis et al. found that not all experimental approaches that have been used so far might be suitable for a reliable spatial analysis of membrane degradation. Confocal Raman microscopy as a post mortem analysis tool to investigate the degradation of ionomer membranes can provide valuable data of the spatial distribution of ageing. In future, this method can complement established techniques in order to elucidate degradation mechanisms and factors that influence membrane ageing.

Conclusions

In this work we investigated the capabilities of confocal Raman microscopy for the analysis of ionomers that are used as proton exchange membranes in fuel cells. We developed a novel approach to use confocal Raman microscopy as a simple and non-destructive tool to quantify the EW of Nafion. Highly standardized measurement settings are required and a device-specific calibration curve has to be prepared in order to calculate the EW of an ionomer sample reliably. Our approach reaches a significantly higher accuracy than other published chemical methods, with a 95% confidence interval of ±13 g mol\(^{-1}\) at an EW of 1000 g mol\(^{-1}\).

Further, confocal Raman microscopy offers the power of a depth-resolved analysis of multi-layered and aged ionomer membranes. To demonstrate the spatial resolution of confocal Raman microscopy, we used our novel measurement method to investigate the application-relevant issue of membrane degradation. We evaluated the degradation of a Nafion NR-211 membrane within a PEMFC. Our results show that upon an OCV hold, as an accelerated stress test, the ionomer membrane exhibited substantial thinning which was accompanied by a clear increase in the EW. Both are signs of chemical-mechanical membrane degradation\(^{15,16}\) and their onsets could be observed already after short timespans of the employed stress test protocol. Electrochemical characterization of the PEMFC confirmed signs of ageing in agreement with results obtained by confocal Raman microscopy. While the pristine membrane showed a homogeneous EW distribution, the analysis of aged samples with confocal Raman microscopy revealed increasing differences in the xy-plane as well as along the z-axis. Most pronounced EW increases of the membrane were observed closer to the anode side than the cathode side of the membrane. The fact that the highest EW values were found close to but not directly at the anode was attributed to the degradation mechanism, which is supposed to remove sidechains of the ionomer first, followed by the decomposition of the polymer backbone.

In summary, confocal Raman microscopy is a promising tool for quantitative ionomer characterization. It offers applications as a quality control for pristine membranes and as a quantitative analysis tool to obtain 3D information of degraded membranes. Ion exchange membrane characterization options with confocal Raman microscopy are manifold and are not limited to Nafion and fuel cells, but also include other PFSAs and different ionomer types for applications such as electrolys or redox-flow batteries.

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