Determination of the through-plane profile of vanadium species in hydrated Nafion studied with micro X-ray absorption near-edge structure spectroscopy – proof of concept

Christian Lutz,* Sven Hampel,* Sabine Beuermann, Thomas Turek, Ulrich Kunz, Jan Garrevoet, Gerald Falkenberg and Ursula Fittschen*

*Institute of Inorganic and Analytical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Straße 4, Clausthal-Zellerfeld 38678, Germany, Institute of Technical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Straße 4, Clausthal-Zellerfeld 38678, Germany, Institute of Chemical and Process Engineering Chemistry, Clausthal University of Technology, Leibnizstraße 17, Clausthal-Zellerfeld 38678, Germany, Energie-Forschungszentrum Niedersachsen, Am Stollen 19A, Goslar 38640, Germany, and Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, Hamburg 22607, Germany. *Correspondence e-mail: ursula.fittschen@tu-clausthal.de

Vanadium-ion transport through the polymer membrane results in a significant decrease in the capacity of vanadium redox flow batteries. It is assumed that five vanadium species are involved in this process. Micro X-ray absorption near-edge structure spectroscopy (micro-XANES) is a potent method to study chemical reactions during vanadium transport inside the membrane. In this work, protocols for micro-XANES measurements were developed to enable through-plane characterization of the vanadium species in Nafion 117 on beamline P06 of the PETRA III synchrotron radiation facility (DESY, Hamburg, Germany). A Kapton tube diffusion cell with a diameter of 3 mm was constructed. The tube diameter was chosen in order to accommodate laminar flow for cryogenic cooling while allowing easy handling of the cell components by hand. A vertical step size of 2.5 μm and a horizontal step size of 5 μm provided sufficient resolution to resolve the profile and good statistics after summing up horizontal rows of scan points. The beam was confined in the horizontal plane to account for the waviness of the membrane. The diffusion of vanadium ions during measurement was inhibited by the cryogenic cooling. Vanadium oxidation, e.g. by water radiolysis (water percentage in the hydrated membrane ~23 wt%), was mitigated by the cryogenic cooling and by minimizing the dwell time per pixel to 5 ms. Thus, the photo-induced oxidation of V^{3+} in the focused beam could be limited to 10%. In diffusion experiments, Nafion inside the diffusion cell was exposed on one side to V^{3+} electrolyte and on the other side to VO_2^{+}. The ions were allowed to diffuse across the through-plane orientation of the membrane during one of two short defrost times (200 s and 600 s). Subsequent micro-XANES measurements showed the formation of VO_2^{+} from V^{3+} and VO_2^{+} inside the water body of Nafion. This result proves the suitability of the experimental setup as a powerful tool for the determination of the profile of vanadium species in Nafion and other ionomeric membranes.

1. Introduction

Due to their theoretically unlimited capacity and their long life cycle, redox flow batteries (RFB) are promising candidates for short- and long-term energy storage of wind, water and solar power. The most investigated and advanced RFB system is the vanadium redox flow battery (VRFB) (Skyllas-Kazacos et al., 1986; Weber et al., 2011; Skyllas-Kazacos et al., 2013; Noack et al., 2015; Lourenssen et al., 2019).

The VRFB consists of two half-cells separated by a polymer electrolyte membrane (PEM). Every half-cell is connected to
an electrolyte tank. The negative electrolyte (NE) consists of the redox-active vanadium species V^{2+}/V^{3+} and the positive electrolyte (PE) consists of VO_2+/VO_2^+, both dissolved in a 4 M sulfuric acid solution. During charging, the electrolytes are pumped continuously through the half-cells, reducing V^{3+} to V^{2+} in the NE and oxidizing VO_2^+ to VO_2^+ in the PE. For discharging, the reactions are reversed (Noack et al., 2015; Lourenssen et al., 2019).

The performance of the VRFB is mainly determined by the properties of the PEM such as its permeability (Kusoglu & Weber, 2017). Ideally, it separates the reactive vanadium species and only enables proton conduction. However, the most investigated and used membrane, Nafion, has poor ion selectivity (Schwenzer et al., 2011). Therefore, vanadium ions are transported through the membrane, often referred to as vanadium crossover. The consequences of this are an imbalance of the vanadium concentration between the two half-cells, self-discharge reactions, and a mainly osmosis-driven water transport. These processes result in a decrease in the capacity over time (Zawodzinski et al., 2010; Schafner et al., 2021). To make the VRFB more viable and practicable, it is necessary to understand the transport processes through and inside the membrane.

In the last few years, several groups have shown that in a VRFB operated with Nafion as separator, the vanadium concentration increases in the PE and decreases in the NE (Sun et al., 2010; Luo et al., 2012). In addition, experimental results and macroscopic observations have been implemented in membrane transport models. VRFB models have been developed by e.g. Knehr and co-workers (Knehr et al., 2012; Knehr & Kumbur, 2012; Agar et al., 2013) and Won et al. (2015). Both models are based on the Nernst–Planck equation and consider diffusion, migration and convection. According to their results, the transport is dominated by diffusion. However, the models disagree on the magnitude of the respective transport mechanisms. Redox reactions between the transported vanadium species inside the membrane could be the neglected factor responsible for the deviations of the different models. In our previous work, a proof for redox reactions in the water body of Nafion was found by studying vanadium species in-plane via XANES on the BESSY II BAMline (Lutz, Hampel et al., 2021). The formation of the vanadium dimer V_2O_4^{3+} from VO_2^+ and VO_2^+ in the PE [K = 0.8 M^-1 (Blanc et al., 1982)] is another reaction for which we found evidence of occurrence inside the water body of the ionomeric membrane; although the equilibrium constant is quite small, the unique conditions in the water reservoir seem to favor the dimer formation.

Model calculation can predict the profiles of vanadium species once the diffusion coefficients and reaction rates are known. Nonetheless, experimental data for through-plane vanadium transport are necessary to evaluate the validity of the models and to prove that chemical reactions contribute to the transport.

UV–Vis spectroscopy has been used to probe membranes directly (Vijayakumar et al., 2011). However, the determination of the vanadium species’ composition in the PE with UV–Vis spectroscopy is biased due to the formation of a strongly absorbing dimer (Blanc et al., 1982). Jia et al. (2014) have shown that synchrotron XANES is suitable for the in situ speciation of vanadium in the NE and PE. Compared with UV–Vis, the XANES spectrum of the V K-edge (5465 eV) is more specific to the vanadium oxidation state. In the literature, the speciation of vanadium inside PEMs has rarely been addressed and is no doubt more challenging. In our previous work, we showed that laboratory-based and synchrotron XANES are suitable for the speciation of vanadium inside a membrane (Lutz & Fittschen, 2020; Lutz, Breuckmann et al., 2021). Laboratory-based XANES is associated with quite a long measurement time (~5 h per spectrum) and a poor spatial resolution with a probe diameter of the order of millimetres.

The Nafion 117 membrane studied here has a thickness of approximately 180 μm. Hence, the pixel size should not exceed 5 μm to resolve the profiles of the vanadium species. Accordingly, the micro-XANES experiments were performed at a synchrotron radiation source, namely at PETRA III (DESY, Hamburg, Germany). The undulator of the hard X-ray microprobe beamline P06 generates a high-brilliance beam. Even though the X-ray optics, such as the Si(111) crystal monochromator, apertures and filters, and absorption in the 1.5 m long air path between the exit window and the sample eliminate a large fraction of the radiation, the photon flux on the sample is still 6 × 10^8 photons s^-1 (the flux without air absorption would be about 2 × 10^10 photons s^-1). Since the X-ray beam is focused to an area of 500 nm × 5 μm (V × H, FWHM), the photon flux density is about 2.9 × 10^14 photons s^-1 mm^-2.

It is well known that with increasing photon flux density, the extent of radiation damage increases (George et al., 2012). Because of this and the high water content of the sample (~23 wt%), radiation damage by photo-oxidation and water radiolysis is to be expected if no countermeasures are taken. During water radiolysis, reactive species form e.g. hydrated electrons (e_{aq}^-) and hydroxyl radicals (HO·). Subsequently, they may react with the vanadium ions (Jonah, 1995). Mesu et al. (2007) studied the influence of X-ray irradiation ( photon flux density 1.7 × 10^{14} photons s^{-1} mm^{-2}) on organic copper complexes in aqueous solution during XANES analysis. According to their results, the copper changed oxidation state from 2+ to 0 due to water radiolysis. The energy of the Cu K-edge shifted to lower energies and the white line decreased. Similar phenomena were observed by George et al. (2012) and Kubin et al. (2018). Metal ions surrounded by organic ligand molecules, e.g. t-histidine in an aqueous solution studied by Mesu et al., and metal ions at the active centers of hydrated proteins described by George et al., have quite similar chemical surroundings to vanadium ions inside the water body of the PEM. Since the vanadium ions studied here are dissolved in the water body system of the PEM surrounded by the sulfonic acid groups of the polymer, species changes due to reaction with hydrated electrons (e_{aq}^-) and hydroxyl radicals (HO·) comparable with those found in hydrated protein systems are plausible.
It should be noted that radiation damage is not only generated along the track of the primary photon beam through the sample but also by secondary effects like X-ray fluorescence and electron showers due to photoelectrons and Auger electrons (Chapman et al., 2014). The electron showers are confined to some 10 nm around the primary-beam track for the current low X-ray energy condition (Stuckelberger et al., 2017). The V K-edge X-ray fluorescence (excited for primary-beam energy above the vanadium absorption edge) can transmit through the sample a few 100 μm in all directions, but is comparably weak because of the low vanadium concentration inside the Nafion (~0.5 wt%) (Lutz, Breuckmann et al., 2021). Radiation damage to Nafion hydrated with vanadium ions was not observed in laboratory-based XANES (Lutz & Fittschen, 2020). Further experiments determining species stability with an unfocused beam at BESSY II (photon flux density $2.5 \times 10^8$ photons s$^{-1}$ mm$^{-2}$) show that small amounts of V$^{3+}$ are oxidized to VO$^{2+}$ after quite a long irradiation time. According to the results, 5% of the V$^{3+}$ was oxidized after 200 min and at the end of the measurements (700 min) 12% was oxidized (Lutz, Hampel et al., 2021). The photon fluence for the setup on the BAMline was about $1.4 \times 10^9$ photons mm$^{-2}$. Since the focused beam on P06 delivers a considerably higher X-ray dose, radiation damage is expected to occur after an exposure time of some milliseconds (photon fluence $3.1 \times 10^{13}$ photons mm$^{-2}$).

In this study, we describe the experimental procedures found to be suitable to study the profile of the vanadium species in Nafion 117. The experimental conditions provide a sufficient vertical spatial resolution and suitable statistics to determine the species but mitigate species alteration (radiation damage) and ion diffusion during measurements. The required spatial resolution and suitable photon flux were achieved by focusing the beam to 500 nm × 5 μm ($V \times H$). The small vertical focus size was chosen to enable spatial resolution along the profile direction. The limitation of the horizontal beam size enables the correction of potential waviness of the sample.

The radiation damage was reduced by keeping the beam horizontally wide (perpendicular to the profile) and the measurement time short (5 ms). The sample was cryogenically cooled to $\sim$120 K. Due to the low temperature, diffusion processes are inhibited (Ilett et al., 2019). The minimization of thermal motion is essential as it fixes the profile of the vanadium species. It also freezes the reactive, which are formed from potential water radiolysis. Thereby, the chemical oxidation of the vanadium ions by e.g. radicals is inhibited (Le Caër, 2011; Warkentin & Thorne, 2010).

In this work, a diffusion cell was constructed which allowed through-plane diffusion from two sides as well as efficient cooling by the Oxford Cryostream. With this cell, profiles of the vanadium species in Nafion 117 membranes could be obtained with a resolution of 2.5 μm. The results show that redox reactions inside Nafion take place during through-plane diffusion. These procedures could perhaps be adapted for the investigation of other ionomeric membranes or X-ray sensitive samples. Furthermore, the obtained experimental data can be used to complete existing VRFB models with respect to transport processes and ion–ion interactions inside the PEM.

2. Experimental
2.1. Chemicals

Nafion 117 was obtained from Chemours (thickness of the dry membrane 178 μm, equivalent weight 1100 g n(SO$_3$)$_2$)$^{-1}$; Wilmington, Delaware, USA). Sulfuric acid (95%–97%) and hydrogen peroxide (30%) were purchased from Merck (for analysis; Darmstadt, Germany). Ultrapure water was generated by a Veolia Elga Purelab Flex 4 water purification system (conductivity 0.055 μS cm$^{-1}$; Paris, France). Vanadium electrolytes were electrochemically converted from V$^{3+}$/VO$^{2+}$ electrolyte (vanadium concentration 1.6 M, sulfuric acid concentration 4 M; Gesellschaft für Elektrometallurgie mbH, Nürnberg, Germany) using an in-house VRFB cell described by Lutz & Fittschen (2020). The composition of the vanadium electrolyte was evaluated using a UV–Vis spectrometer (Jasco V-670; Pfungstadt, Germany). The NE was analyzed using a 1 mm quartz cuvette (Hellma, Müllheim, Germany) and the PE using a 0.1 mm flow-through quartz cuvette (Hellma, Müllheim, Germany).

2.2. Membrane pretreatment and preparation

Nafion was pretreated similar to the procedure described by Tang et al. (2013). Nafion was held sequentially in 3% hydrogen peroxide, ultrapure water, 1 M sulfuric acid and ultrapure water. Every step was performed for 1 h at 353 K.

Pretreated Nafion 117 was immersed in 1.6 M electrolyte, either V$^{3+}$, VO$^{2+}$ or VO$_2$+, for 72 h at room temperature. The membrane was extracted from the electrolyte and superficial electrolyte was removed using a laboratory wipe. A membrane piece with a diameter of 2.5 mm was then stamped out. The membrane piece was placed in a Kapton tube (outer diameter 3 mm, inner diameter 2.94 mm; Goodfellow, London, UK) between two layers of dry filter paper (diameter 2.5 mm, thickness 0.17 mm; Macherey-Nagel, Düren, Germany). The setup was fixed between a neodymium magnet with a diameter of 2 mm at the top (nickel-coated; magnets4you, Lohr am Main, Germany). A photograph and render images of the described sample holder are shown in Figs. 1(a)–1(c). For the measurements, the samples were mounted on an $xyz$ piezo stage.

The diffusion cell was prepared similarly to the membrane sample holder. The differences are that a pretreated and vanadium-free membrane was placed between a filter paper soaked with VO$_2^+$ (diameter 2 mm) at the bottom and a filter paper soaked with V$^{3+}$ (diameter 2 mm) at the top. Both soaked filter papers were surrounded by a larger dry filter paper (diameter 2.5 mm) to prevent leakage of the vanadium electrolyte. In Figs. 1(d) and 1(e), render images of the diffusion cell are presented. For every diffusion experiment, a fresh cell was prepared. The cell was assembled in liquid nitrogen, removed, and held at room temperature for either
200 or 600 s. During this time, the electrolyte was allowed to defrost and vanadium ions were able to diffuse through the membrane. After the defined time period, the membrane was again frozen in liquid nitrogen to stop the diffusion and freeze the profile of the vanadium species. Finally, the frozen samples were mounted on the piezo sample stage with cryogenic cooling by an Oxford Cryostream.

2.3. Instrumentation

Synchrotron XANES measurements in fluorescence mode were performed on the hard X-ray micro-/nano-probe beamline P06 (PETRA III, DESY, Hamburg, Germany) (Schroer et al., 2010). The beam was monochromated using an Si(111) double-crystal monochromator (DCM) with an energy resolution of $\Delta E/E = 2 \times 10^{-4}$. For higher harmonic suppression, a pair of horizontally deflecting Si mirrors was used. The incoming beam was monitored by a 33 mm long ionization chamber filled with dry nitrogen. Afterwards, the beam was focused by a Kirkpatrick–Baez mirror system to a size (FWHM) of 0.5 $\mu$m $\times$ 5 $\mu$m (V $\times$ H). The characteristic fluorescence radiation was measured with a 50 mm$^2$ SII Vortex EM Si-drift detector (Hitachi High-Tech, Chatsworth, California, USA) in 135° geometry, selected to minimize shading effects. According to absorption measurements and calculations with XOP (ESRF, Grenoble, France), the attenuation length of the primary beam in hydrated Nafion is of the order of 300 $\mu$m and the information depth of the vanadium signal is of the order of 100 $\mu$m. The sample was mounted on a three-axis piezo scanner system (Aerotech, Pittsburgh, Pennsylvania, USA) on top of a hexapod (Newport, Irvine, California, USA) for alignment. The piezo scanner system has a working range of 500 $\mu$m for every axis. In addition, the sample was cooled to 120 K from above using an Oxford Cryostream Cooler 700 (Oxford, United Kingdom). Because of the cooling, the sample was stabilized against water radiolysis and diffusion of the vanadium ions was stopped. A digital microscope equipped with an HV-Z50W lens (Keyence, Osaka, Japan) was installed between the sample and the Kirkpatrick–Baez mirror system to get a visual overview. A top-view schematic diagram of the setup is shown in Fig. 2.

All measurements were performed in lateral 2D scan mode with continuous movement of the fast axes (sweep scan) and with the energy as the third (slowest) axis. In both sweep scans, the pixel size was 2.5 $\mu$m $\times$ 5 $\mu$m. The vertical fast-axis scan speed was 0.5 mm s$^{-1}$ and the horizontal fast-axis scan speed was 1 mm s$^{-1}$. The acquisition time per 2.5 $\mu$m $\times$ 5 $\mu$m pixel for both scans was 5 ms. However, because of the actual beam

![Figure 1](image1.png)

(a) A photograph of the sample holder for the measurement of Nafion. (b) and (c) Render images of the sample holder for the measurement of Nafion (reference). (b) normal view and (c) exploded view. (d) and (e) Render images of the sample holder for the measurement of Nafion (diffusion). (d) normal view and (e) exploded view. In all panels, (1) is the neodymium magnet (diameter 2 mm), (2) two layers of dry filter paper, (3) Nafion 117 soaked with vanadium electrolyte (in the rendering soaked with green V$^{3+}$ electrolyte), (4) neodymium magnet (diameter 3 mm), (5) Kapton tube, (6) one layer of dry filter paper, (7) one layer of filter paper soaked with V$^{3+}$ electrolyte, (8) hydrated Nafion 117 (vanadium-free) and (9) one layer of filter paper soaked with VO$_2^+$ electrolyte.

![Figure 2](image2.png)

Top-view schematic diagram of the experimental setup at DESY. (1) is the synchrotron X-ray beam, (2) ionization chamber ($I_0$), (3) Kirkpatrick–Baez mirror system, (4) microscope, (5) sample, (6) Si-drift detector, (7) X-ray fluorescence and (8) excited volume of the sample. Distances are not to scale.
dimensions of 500 nm × 5 μm only a sixth of the area was illuminated during the horizontal sweep scans, resulting in a higher local dose compared with the vertical sweep scan, where the entire pixel was illuminated during the same time interval. Hence, the entire area is irradiated homogeneously during vertical sweep scans, while for horizontal scans, between every horizontal line with a height of 500 nm a non-irradiated gap of 2000 nm is present (see Figs. 3 and 4). This results in the same total X-ray dose per scan or pixel for both sweep scans, but the local X-ray dose is approximately six times higher for horizontal sweep scans than for vertical sweep scans.

In Figs. 3 and 4, the vertical and horizontal sweep scans are illustrated. During vertical sweep scans, an area with beam dimensions of 500 nm × 5 μm is irradiated for 1.68 ms. It experiences an increasing flux for 0.84 ms and a gradually decreasing flux for further 0.84 ms. In total, the area experiences a dose given by the full flux time of 0.84 ms. Analogous to vertical sweep scans, an area of 500 nm × 5 μm is irradiated for 10 ms during horizontal sweep scans and experiences a dose given by the full flux time of 5 ms.

The V K-edge spectra were obtained in the energy range 5413–5711 eV. The scan protocol included a sufficient number of data points in the pre- and post-edge region for the normalization. In addition, the pre-edge peak was probed with 3D stacks, either the vertical or horizontal sweep scan pixels of one row were extracted, added up and saved in an ASCII file separately. Then, the added up X-ray spectra and the number of vertical steps and the number of horizontal steps, are given in Table 1.

Table 1
Summary of the scan settings for all measured samples.
The columns give the sweep scan direction, the number of added up XANES spectra, the number of vertical steps (beam height 500 nm, step height 2.5 μm) and the number of horizontal steps (beam width 5 μm, step width 5 μm).

| Sample                      | Sweep scan direction | No. of added up XANES spectra | No. of vertical steps | No. of horizontal steps |
|-----------------------------|----------------------|-------------------------------|-----------------------|-------------------------|
| N117 + V3+ (reference)      | Vertical             | 60                            | 60                    | 60                      |
| N117 + V3+                  | Vertical             | 60                            | 60                    | 60                      |
| N117 + VO2+ and VO2− (reference) | Vertical         | 60                            | 60                    | 2                       |
| N117 diffusion experiments  | Vertical             | 60                            | 100                   | 60                      |

obtained from Nafton 117 soaked with a single vanadium electrolyte (V3+, VO2+ or VO2−) for reference and from Nafton 117 subjected to diffusion experiments. A vanadium foil (thickness 5 μm; Exafs Materials, Danville, California, USA) served as reference.

The fluorescence spectra were obtained by integrating the fluorescence over 2.5 μm of the vertical sweep scan and over 5 μm of the horizontal sweep scan. The V Kα signal (I) (region of interest) was then added up for every sweep scan pixel and every energy individually and this resulted in a 3D image stack (TIFF files). Simultaneously, the incoming beam intensity (I0) was measured in the ion chamber and also saved in a 3D stack. From both 3D stacks, either the vertical or horizontal sweep scan pixels of one row were extracted, added up and saved in an ASCII file separately. Then, the added up X-ray spectra (1D scan energy stack) were processed using ATHENA (Ravel & Newville, 2005). A linear combination fit (LCF) in the range 5464–5474 eV (pre-edge peak of V K-edge) was performed to assign the vanadium species fractions.

In general, the XANES spectra of one horizontal level (N117 + V3+ horizontally, reference spectra of V3+ and diffusion experiment) were added up for better statistics. The reference spectra of VO2+ and VO2−, and the spectra of N117 + V3+ scanned vertically, were obtained by adding up 60 XANES spectra in the middle of the membrane. The scan settings for all measurements, including the sweep scan direction, the number of added up XANES spectra, the number of vertical steps and the number of horizontal steps, are given in Table 1.

3. Results and discussion
3.1. Vanadium speciation in Nafton 117
In this work, a new approach for the determination of the through-plane profile of vanadium species in Nafton using micro-XANES was investigated. However, the speciation of vanadium inside hydrated membranes can easily be hampered by species alteration caused by the brilliant synchrotron microbeam. Hence, the experimental design needed to optimize for (i) minimized alteration of the vanadium species,
Here, \( N_0 \) is the photon flux, determined during the measurements (6 \( \times 10^8 \) photons s\(^{-1}\)), \( h \nu \) is the energy of the photons (5413–5711 eV), \( L_a \) is the attenuation length (300 \( \mu \)m), \( \rho \) is the density of the sample (1.98 g cm\(^{-3}\)), \( A \) is the irradiated area (0.5 \( \mu \)m \( \times \) 5 \( \mu \)m) and \( t \) is the exposure time. Accordingly, the local X-ray dose for vertical sweep scans is \( 3.79 \times 10^5 \) Gy and that for horizontal sweep scans is \( 2.26 \times 10^5 \) Gy. In Fig. 5, exemplary V\( K \)-edge spectra for vertical (red dashed line) and horizontal (black line) sweep scans are shown.

The spectra of V\(^{3+} \) measured using vertical and horizontal sweep scans differ significantly in the pre-edge peak region. The pre-edge peak intensity in the spectrum measured horizontally is nearly twice that of the pre-edge peak intensity in the spectrum measured vertically. However, the data suggest that the oxidation of V\(^{3+} \) occurs already during the vertical sweep scan. Extrapolating from the pre-edge peak intensity, 10% of the V\(^{3+} \) are oxidized to VO\(^{2+} \) (32.5% in the horizontal sweep scan). The comparison illustrates that, besides the already applied cryogenic cooling and 5 \( \mu \)m broad beam, the exposure time must be kept to a minimum.

Despite the radiation damage, the results prove the reaction of VO\(_2^+\) with V\(^{3+} \) to VO\(^{2+} \) in Nafion and allow the recording of through-plane species profiles, showing e.g. a plateau of constant 1:1 VO\(_2^+\) to VO\(^{2+} \) ratio. The results will be discussed in the following section (Section 3.2). However, for future studies, it is advisable to suppress radiation-induced oxidation even further, so that the profiles of the vanadium species show an even smaller bias. This will be realized by minimizing the X-ray dose. Possibly, a rotation stage instead of an xyz stage can be used and the complete circumference of the Kapton tube (9.4 mm) be made available for scanning. This would allow the collection of every data point from a fresh area not irradiated previously, which would lead to an X-ray dose 127 (the number of energy points) times smaller. In view of the information depth of 100 \( \mu \)m (the V\( K \) X-ray fluorescence attenuation length in Nafion is similar to the attenuation length of the primary beam due to the low vanadium concentration) and no overlap between already irradiated volume, the circumference provides ~1600 data points. Multiple irradiation of volume can be excluded, since the beam penetrates only a fraction of the sample radius. In addition, the scanning speed could be enhanced by increasing the solid angle of detection (e.g. Maia detector). Hence, shorter acquisition times are possible, leading to an additional reduction in the local dose.

The reference spectra were obtained from Nafion hydrated with a single vanadium species, taking the precautions described above. In Fig. 6, the spectra of Nafion hydrated with V\(^{2+} \), VO\(^{2+} \) and VO\(_2^+\) electrolytes are shown.
The spectra of Nafion hydrated with VO\(_{2}^{+}\) and VO\(_{2}^{+}\) electrolytes are comparable with those obtained from in situ measurements of vanadium electrolyte by Jia et al. (2014) taken at the Advanced Photon Source (APS), laboratory-based XANES measurements performed by Lutz & Fittschen (2020), and measurements of Nafion hydrated with vanadium ions by Lutz, Breuckmann et al. (2021) at BESSY II. As expected, the pre-edge region differs significantly for the different vanadium species. The spectrum of VO\(_{2}^{+}\) displays a prominent pre-edge peak at 5470 eV and the pre-edge peak of VO\(_{2}^{+}\) appears at 5471.2 eV. As discussed above, the spectrum of V\(^{3+}\) differs in the pre-edge region compared with the literature. However, both the intensity and the energy of the pre-edge peak allow for distinguishing between the vanadium species. In this work, the composition was determined by applying LCF on the pre-edge peak in the energy range 5464–5474 eV. Although the main edge energy increases with higher oxidation state, it was not used for the species determination because (i) more pre- and post-edge energy steps would have been necessary to minimize errors and, maybe most important, (ii) the pre-edge peak does not suffer from self-absorption of the white line, which occurs in fluorescence mode when a sample exceeds the critical thickness. The analyzed samples have an infinite thickness in our experiment and the information depth is in the region of 100 μm.

3.2. Determination of in-plane vanadium profile in Nafion 117

To study reactions between PE and NE reactive species, the membrane is brought into contact with V\(^{3+}\) from the top and with VO\(_{2}^{+}\) from the bottom, and the ions are allowed to be transported through the plane of the membrane. The advantage of this simple electrolyte combination – in actual VRFBs V\(^{2+}\) would also be present in the NE and VO\(_{2}^{+}\) in the PE – is that the formation of VO\(_{2}^{+}\) unambiguously proves redox reactions occur inside the water body of the membrane. In Fig. 7, the vanadium profiles are shown for experiments after diffusion times of (a) 200 s and (b) 600 s. In addition, the counts of the edge (difference in counts before and after the edge) used to estimate the vanadium concentration and the R factor as a goodness-of-fit parameter are displayed on the left and right, respectively. The R factor was calculated by analogy with Gaur & Shrivastava (2015) with the following formula:

\[
R = \frac{\sum_i (\text{data}_i - \text{fit}_i)^2}{\sum_i \text{data}^2_i}.
\]

The thickness of the membrane in the diffusion cell is ~150 μm and is indicated in Fig. 7 with the gray shaded areas. The adjacent filter papers soaked with vanadium electrolyte (0 μm: V\(^{3+}\); 250 μm: VO\(_{2}^{+}\)) were included in the scans (un-colored area in Fig. 7). After 200 s [Fig. 7(a)], the soaked filter paper shows a high vanadium concentration, which decreases towards the membrane. The membrane has a significantly lower vanadium concentration than the filter papers.

After 200 s [Fig. 7(a)], the V\(^{3+}\) fraction in the filter paper soaked with V\(^{3+}\) electrolyte and the first ~10 μm into the membrane is 90% (10% is already oxidized due to radiation damage during the measurements, as discussed above). Further into the membrane, the V\(^{3+}\) decreases non-linearly towards the other side of the membrane. A similar profile is observed on the side exposed to VO\(_{2}^{+}\). However, V\(^{3+}\) seems to have diffused faster than VO\(_{2}^{+}\). This result suggests that the diffusion coefficient of V\(^{3+}\) is larger than that of VO\(_{2}^{+}\). Nevertheless, it should be taken into account that the transport of V\(^{3+}\) is additionally supported by gravity. Both vanadium ion fronts meet at approximately 175 μm and form VO\(_{2}^{+}\). Here, the highest percentage of newly formed VO\(_{2}^{+}\) is found. It decreases towards both ends of the membrane.

To evaluate the correctness of the data obtained from the LCF, the R factor was calculated. The smaller the R factor, the better the fit matches the experimental data. After 200 s, the areas with a high vanadium concentration (electrolyte reservoirs) have a small R factor of the order of 0.02 (VO\(_{2}^{+}\)) to 0.05 (V\(^{3+}\)). In contrast, the R factor is significantly higher for the fit of data from inside the membrane. With decreasing vanadium concentration, the R factor increases. In particular, the interesting regions where the reactions occur have an R factor larger than 0.15 and therefore a major error. In Fig. 8, the fits and experimental data at positions of 0, 112.5, 187.5 and 250 μm are shown. The fit and the experimental data in the electrolyte reservoir (0 and 250 μm) match well. However, the spectra obtained inside the membrane have a low signal-to-noise ratio (Fig. 8, 112.5 and 187.5 μm).
In general, it is more difficult to distinguish between V$^{3+}$ and VO$_2^+$ than between VO$_2^+$ and VO$_2^{2+}$ because V$^{3+}$ and VO$_2^{2+}$ have the same pre-edge peak energy. In comparison, the determination of the VO$_2^+$ fraction beside VO$_2^+$ has a smaller error because of the unique pre-edge energy of VO$_2^+$ ($\Delta = 1.2 \text{ eV}$). The error during VO$_2^+$ determination is of the order of $\sim 15\%$ for areas of low concentration (150–200 $\mu$m) and decreases with increasing vanadium concentration to less than $\sim 5\%$. According to counting statistics, the limit of detection of VO$_2^+$ beside V$^{3+}$ in the area of low concentration (187.5 $\mu$m) is of the order of $\sim 20\%$. The detection limit decreases in areas of high concentration (0 $\mu$m) down to a value of $\sim 2\%$. In conclusion, the concentrations of the formed VO$_2^+$ are at the detection limit in the 200 s sample. However, the formation of VO$_2^+$ after 600 s [Fig. 7(b)] supports the presence of VO$_2^+$ after 200 s.

After 600 s [Fig. 7(b)], VO$_2^+$ has unambiguously formed inside the membrane and diffused to both ends of the membrane. The determination of the vanadium fraction, especially of the VO$_2^+$ fraction, is more accurate compared with the determination after 200 s because of the quite high vanadium concentration in the whole membrane. Therefore, the $R$ factor is quite low, of the order of 0.02, over the entire profile. In Fig. 9, the fit and experimental data at positions of 0, 112.5, 187.5 and 250 $\mu$m are shown. Compared with the spectra of Fig. 8, the signal-to-noise ratio is higher. According to counting statistics, the limit of detection for VO$_2^+$ beside V$^{3+}$ is of the order of $\sim 4\%$ over the complete scanning range. The determination of VO$_2^+$ beside V$^{3+}$ has an error of $\sim 5\%$.

Additionally, the vanadium species and concentration profile after 600 s on the side exposed to VO$_2^+$ shows no significant differences from the one allowed to defrost for 200 s (200–250 $\mu$m). However, the fraction of VO$_2^+$ and VO$_2^{2+}$ has increased into the membrane towards the V$^{3+}$ reservoir. The VO$_2^+$ percentage increases towards the V$^{3+}$ reservoir from the point where both the V$^{3+}$ and VO$_2^{2+}$ fronts meet. V$^{3+}$ has largely disappeared from the membrane and even from the filter paper. The vanadium ion distribution between 150 and 200 $\mu$m is also noteworthy. It seems that over this entire range the ratio of VO$_2^+$ to VO$_2^{2+}$ is 1:1. It is well known that VO$_2^+$ and VO$_2^{2+}$ form a dimer at high concentrations (Blanc et al., 1982). Probably, this interaction takes place inside the membrane and the newly formed dimer acts like a barrier to the diffusion of VO$_2^{2+}$. Hence, the vanadium concentration and vanadium ion profile do not show significant change. The diffusion coefficient of the dimer, to the best of our knowledge, has not been published yet. Our data suggest that it diffuses much more slowly than the other species.

Another phenomenon is observed after 600 s [Fig. 7(b)]: the filter paper exposed to VO$_2^+$ (250 $\mu$m) has nearly the same vanadium concentration as after 200 s. However, the other side shows a significant change. The concentrations of the filter paper soaked with V$^{3+}$ and the membrane seem to have equilibrated and the V$^{3+}$ electrolyte is depleted into the membrane. In summary, a set of conditions was determined to study through-plane profiles of vanadium species inside Nafion.

4. Conclusions

In this work, it has been shown that synchrotron scanning micro-XANES is a powerful tool for the determination of the vanadium species inside a Nafion membrane. A procedure to study the through-plane profile of the vanadium species in the 180 $\mu$m thick Nafion was developed, allowing for a spatial resolution of 2.5 $\mu$m. The change in vanadium species was minimized by reducing the mobility of reactive species through cryogenic cooling and by minimizing the radiation dose. It was shown that an increase in the exposure time from 1.68 to 10 ms results in an increase in the vanadium ion oxidation from 10% to 35%.

The profiles of vanadium species were obtained using a diffusion cell setup, where Nafion was exposed from one side to V$^{3+}$ electrolyte and from the other side to VO$_2^+$. The profile of the vanadium species was determined after 200 and 600 s. The orientation of the diffusion was through-plane. For quantification, the pre-edge peak intensity and energy were used. After 200 s the spectra show strong evidence that VO$_2^+$ was formed. However, the linear combination fits are less reliable than those after 600 s due to the low vanadium concentration inside the membrane. After 600 s the formation of VO$_2^+$ is evident.

In our previous work, reactions of vanadium ions in the plane of Nafion 117 were observed, albeit with low spatial
resolution (Lutz, Breuckmann et al., 2021). Here, it was shown that this reaction (VO$^{2+}$ is formed from V$^{3+}$ and VO$^{2+}$) and the profiles of vanadium species inside the nanoscopic water body of Nafion in the through-plane orientation can be analyzed with a high spatial resolution.

In future work, the diffusion cell will be used to determine the profiles of vanadium species with a higher time resolution and different vanadium electrolyte combinations. The experimental results will then be compared with model results, and e.g. diffusion coefficients and reaction kinetics will be determined.

Although the radiation damage was reduced here to a level where meaningful profiles were obtained, the aim of future studies is to reduce the alteration of species further and with that increase the detection efficiency. Therefore, the radiation dose could be minimized by adding a rotation stage and substituting the horizontal scan by a rotational scan for which the Kapton tube needs to be carefully centered. This design is advantageous, because the dose would be spread over a 20 times larger area (circumference of the capillary). When exposed only to a low dose, the same sample can be used for multiple defrosting/diffusion–freezing cycles. In addition, the scanning speed can be increased even more by increasing the solid angle of detection.

Acknowledgements

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III and we would to thank Jan Garrevoet and Gerald Falkenberg for assistance using the microprobe station of the beamline P06.

Funding information

The following funding is acknowledged: Deutsches Elektronen-Synchrotron (grant No. I-20191415 to Christian Lutz, Sven Hampel and Ursula Fittschen).

References

Agar, E., Knehr, K. W., Chen, D., Hickner, M. A. & Kumbur, E. C. (2013). Electrochim. Acta, 98, 66–74.
Blanc, P., Madic, C. & Launay, J. P. (1982). Inorg. Chem. 21, 2923–2928.
Chapman, H. N., Caleman, C. & Timineau, N. (2014). Philos. Trans. R. Soc. B, 369, 20130313.
Gaur, A. & Shrivastava, B. D. (2015). Ref. J. Chem. 5, 361–398.
George, G. N., Pickering, I. J., Pushie, M. J., Niemaber, K., Hackett, M. J., Ascone, I., Hedman, B., Hodgson, K. O., Atiken, J. B., Levina, A., Glover, C. & Lay, P. A. (2012). J. Synchrotron Rad. 19, 875–886.
Giuli, G., Paris, E., Mungall, J., Romano, C. & Dingwell, D. (2004). Am. Mineral. 89, 1640–1646.
Howells, M. R., Beetz, T., Chapman, H. N., Cui, C., Holton, J. M., Jacobsen, C. J., Kirz, J., Lima, E., Marchesini, S., Miao, H., Sayre, D., Shapiro, D. A., Spence, J. C. H. & Starodub, D. (2009). J. Electron Spectrosc. Relat. Phenom. 170, 4–12.
Illett, M., Brydson, R., Brown, A. & Hondon, N. (2019). Micron, 120, 35–42.
Jia, C., Liu, Q., Sun, C.-J., Yang, F., Ren, Y., Heald, S. M., Liu, Y., Li, Z.-F., Lu, W. & Xie, J. (2014). ACS Appl. Mater. Interfaces, 6, 17920–17925.
Jonah, C. D. (1995). Radiat. Res. 144, 141–147.
Knehr, K. W., Agar, E., Dennison, C. R., Kalidindi, A. R. & Kumbur, E. C. (2012). J. Electrochem. Soc. 159, A1446–A1459.
Knehr, K. W. & Kumbur, E. C. (2012). Electrochem. Commun. 23, 76–79.
Kubin, M., Kern, J., Guo, M., Källman, E., Mitzner, R., Yachandra, V. K., Lundberg, M., Yano, J. & Wernet, P. (2018). Phys. Chem. Chem. Phys. 20, 16817–16827.
Kusoglu, A. & Weber, A. Z. (2017). Chem. Rev. 117, 987–1104.
Le Caër, S. (2011). Water, 3, 235–253.
Lourenssen, K., Williams, J., Ahmadpour, F., Clemmer, R. & Tasnim, S. (2019). J. Energ. Storage, 25, 100844.
Luo, Q., Li, L., Nie, Z., Wang, W., Wei, X., Li, B., Chen, B. & Yang, Z. (2012). J. Power Sources, 218, 15–20.
Lutz, C., Breuckmann, M., Hample, S., Kreyenschmidt, M., Ke, X., Beuermann, S., Schafer, K., Turek, T., Kunz, U., Buzanich, A. G., Radtke, M. & Fittschen, U. E. A. (2021). Membranes (Basel), 11, 576.
Lutz, C. & Fittschen, U. E. A. (2020). Powder Diffir. 35, S24–S28.
Lutz, C., Hample, S., Ke, X., Beuermann, S., Turek, T., Kunz, U., Guillerme Buzanich, A., Radtke, M. & Fittschen, U. E. A. (2021). J. Power Sources, 483, 229176.
Mesu, J. G., Beale, A. M., de Groot, F. M. F. & Weckhuysen, B. M. (2007). AIP Conf. Proc. 882, 818–820.
Moretti, A., Giuli, G., Nobili, F., Trapananti, A., Aquilanti, G., Tossici, R. & Marassi, R. (2013). J. Electrochem. Soc. 160, A940–A949.
Noack, J., Roznyatovskaya, N., Herr, T. & Fischer, P. (2015). Angew. Chem. Int. Ed. 54, 9776–9809.
Ravel, B. & Newville, M. (2005). J. Synchrotron Rad. 12, 537–541.
Schafer, K., Becker, M. & Turek, T. (2021). J. Appl. Electrochem. 51, 1217–1228.
Schoer, C. G., Boye, P., Feldkamp, J. M., Patommel, J., Samberg, D., Schropp, A., Schwab, A., Stephan, S., Falkenberg, G., Wellenreuther, G. & Reimers, N. (2010). Nucl. Instrum. Methods Phys. Res. A, 616, 93–97.
Schwenzer, B., Zhang, J., Kim, S., Li, L., Liu, J. & Yang, Z. (2011). ChemSusChem, 4, 1388–1406.
Skyllas-Kazacos, M., Menictas, C. & Lim, T. (2013). Electricity Transmission, Distribution and Storage Systems, edited by Z. Melhem, pp. 398–441. Amsterdam: Elsevier.
Skyllas-Kazacos, M., Rychev, M., Robins, R. G., Fane, A. G. & Green, M. A. (1986). J. Electrochem. Soc. 133, 1057–1058.
Stuckelberger, M., Nietzold, T., Hall, G. N., West, B., Werner, J., Niesen, B., Ballif, C., Rose, V., Fenning, D. P. & Bertoni, M. I. (2017). IEEE J. Photovoltaics, 7, 590–597.
Sun, C., Chen, J., Zhang, H., Han, X. & Luo, Q. (2010). J. Power Sources, 195, 890–897.
Tang, Z., Svoboda, R., Lawton, J. S., Aaron, D. S., Papandrew, A. B. & Zawodzinski, T. A. (2013). J. Electrochem. Soc. 160, F1040–F1047.
Vijayakumar, M., Bhuvaneswari, M. S., Nachimuthu, P., Schwenzer, B., Kim, S., Yang, Z., Liu, J., Graff, G. L., Thevuthasan, S. & Hu, J. (2011). J. Membr. Sci. 366, 325–334.
Warkentin, M. & Thorne, R. E. (2010). Acta Cryst. D66, 1092–1100.
Weber, A. Z., Mench, M. M., Meyers, J. P., Ross, P. N., Gostick, J. T. & Liu, Q. (2011). J. Appl. Electrochem. 41, 1137–1164.
Won, S., Oh, K. & Ju, H. (2015). Electrochim. Acta, 177, 310–320.
Wong, J., Lytle, F. W., Messmer, R. P. & Maylotte, D. H. (1984). Phys. Rev. B, 30, 5596–5610.
Zawodzinski, T. A., Derouin, C., Radzinski, S., Sherman, R. J., Smith, V. T., Springer, T. E. & Gottesfeld, S. (1993). J. Electrochem. Soc. 140, 1041–1047.