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Characterization of Chain Conformations in Perfluorosulfonic Acid Membranes using Electron Energy Loss Spectroscopy

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Chain conformations of the perfluorosulfonic acid (PFSA) ionomers: Nafion™ and Aquivion® were investigated with electron energy-loss spectroscopy (EELS) on a 200 kV transmission electron microscope (TEM) equipped with a monochromator. The results were compared with polytetrafluoroethylene (PTFE) to evaluate the effect of the pendant perfluoroether side chains of the ionomers on the structure of the PTFE backbone. Several unique spectroscopic features corresponding to conformational changes were identified in the low-loss region and the fine structures of the carbon K-edge. Results obtained from high-level density function theory (DFT) based electronic structure calculations confirmed the conformational dependence of the EEL spectra of the PFSA ionomers. Comparison with the spectra obtained from the experiments revealed the correlation between the specific side chain chemistry and backbone conformation. This spectroscopic information will allow us to further explore the morphological properties of these materials when combining with additional imaging techniques.

1 Introduction

The need for next generation polymer electrolyte membrane fuel cells (PEMFCs) has driven considerable research effort into the development of novel membrane materials that are highly proton conducting at low temperatures.[1, 2] At present, perfluorosulfonic acid (PFSA) ionomers are the electrolyte of choice in current PEMFCs.[3] PFSA ionomers including the benchmark Nafion™, consist of a hydrophobic poly-tetrafluoroethylene (PTFE) backbone with pendant perfluorinated vinyl ether side chains each terminated with a sulfonic acid group (i.e., $-SO_3H$). The chemistry and molecular structure of the side chains and backbone in PFSAs play a crucial role in determining the hydrated morphology and transport properties especially in the presence of water.[4] Under hydrated conditions, the mesoscale phase separation occurs due to the hydrophobic and hydrophilic segments of the macromolecules. This is mainly due to the aggregation of ionic clusters and the reorganization of the PTFE backbones, which have been investigated by a variety of experimental and modelling approaches.[5-11]

Although numerous studies have been undertaken to elucidate structure-property relationships of PFSA ionomers, much of the research has focused on the characterization of ionic aggregates and their morphology as a function of the degree of hydration. In a previous study, we determined that the length of the side chains can introduce significant conformational changes in the backbone, which potentially affects the formation of the hydrophilic network to facilitate transfer of protons to the aqueous domains.[12, 13] To date, information concerning the conformations of the PTFE chains in these materials is very limited and mainly due to vibrational spectroscopy. Pristine PTFE was examined earlier with infrared (IR) spectroscopy to identify conformational changes during phase transitions and to assess the effects of helix reversal defects on chain orientations.[14, 15] The conformational properties of Nafion membranes were also studied with IR and Raman spectroscopy to better understand the structural evolution of PTFE backbones as a function of hydration.[16] Similar spectroscopic features were found in both crystalline PTFE and Nafion, which indicates the close repeat units in both materials. In addition, the pendant side chains are more likely to introduce additional structural defects and alter the backbone. This effect is believed to be the cause of the disordered short-range structure in Nafion and substantially changes the morphology of the membranes under highly hydrated conditions.

Unlike vibrational spectroscopy and other surface-sensitive techniques, electron energy-loss spectroscopy (EELS) in the transmission electron microscope (TEM) or scanning transmission electron microscope (STEM) is a technique that measures the energy-loss of transmitted electrons during the inelastic interaction with a specimen. The spectroscopic features that arise from the excitation of valence electrons (low-loss) and atomic ionization (core-loss) can be utilized to quantify local chemical composition and structural properties of various polymeric materials.[17-19] On a modern TEM equipped with both a monochromator and a spectrometer, more details in the EELS spectra may be detected with a comparable energy resolution as

X-ray absorption spectroscopy.[20, 21] In addition, spatially resolved EELS combined with imaging techniques such as Dark Field (DF) or Bright Field (BF) in scanning mode allow one to perform an accurate microanalysis of selected areas with controllable beam dose. The resultant spectrum images contain both spatial and spectroscopic information and are especially useful in characterizing complex nanoscale morphologies involving multiple components or phases.

To better understand the structural and optical properties of these membranes, density function theory (DFT) calculations were undertaken to compute energy-loss spectra in both low-loss and core-loss regions. DFT based electronic structure calculations have proven to be an effective way to interpret fine details in spectra and predict material properties.[22, 23] In a recent paper we have characterized PTFE films with EELS, and demonstrated the feasibility of reproducing various features of the valence EELS (VEELS) and energy-loss near-edge structures (ELNES) with DFT calculations.[24] Several unique spectroscopic features were identified in the experiments and were further examined with the calculations when other influential factors such as phase transitions and polarization were considered. Our results showed that the high resolution EELS combined with first principles calculations enables the characterization of chain conformation and orientation for polymers in complex phases.

In the present work, we seek to understand the role of the side chains in determining the conformation of the PTFE backbone of PFSA ionomers. Two types of PFSA membranes with distinct side chains were examined in this study. The manuscript is organized as follows. A brief description of the experimental and simulation methods is given in the first section. This is followed by a discussion of the quantitative analysis of experimental spectra observed in the PTFE and PFSA membranes. The spectroscopic features associated with the backbone conformations of different materials obtained from the electronic structure calculations and compared to experimental results.

2 Experiment and calculation details

Two different PFSA membranes, Nafion and Aquivion, were obtained from DuPont and Solvay Solexis, respectively, in the form of films with thickness in the range of 100 - 150 μm. After careful pre-treatment to remove impurities and conversion to the acid form, the membranes were sectioned by ultramicrotome at temperatures below –80°C following the same methodology as we reported elsewhere.[8] At cryo-temperatures, the thin sections obtained by this method generally retain the properties of the bulk samples and are still within the appropriate thickness range (i.e., 20-30 nm) as required for obtaining high quality EELS. Energy-loss spectra with the highest energy resolution of 0.15 eV (determined by the FWHM of the zero loss peaks) were acquired in a 200 kV Zeiss Libra 200 TEM-STEM equipped with a monochromator in the STEM mode. For the purpose of minimizing overall beam dose and determining the possible resolution, a large area for scanning was selected during the signal collection. To achieve a reasonable signal-to-noise ratio (SNR) in the spectra while not introducing radiation damage that would result in permanent changes to the conformation of the chains, a total of the accumulated electron dose was controlled to be around 10^4 – 10^5 electrons/nm^2 during the acquisition of each spectrum.

In a prior study of PTFE with different conformations, we showed that the one with disordered backbone involving helix-reversal defects is proven to reproduce many spectroscopic features in the low-loss and core-loss regions very well.[24] Hence, we constructed the repeat units of Nafion and Aquivion with the same defected PTFE backbones and replaced one of the fluorine atoms on backbones with the two distinct side chains (see S.1 in supplementary information). The optimized molecular structures of the repeat units of PTFE, Aquivion, and Nafion with defected backbone conformations are illustrated in Figures 1 (a-c), respectively. To evaluate the effect of the side chains, the same sizes of periodic structures (i.e., backbone with 16 CF_2 groups) are used to construct super cells for PTFE and PFSA systems. The helical chains are packed in a hexagonal lattice, where the chains are aligned in the direction of the long axis of the unit cell. We also increase the inter-chain distances to minimize the possible interactions between neighbouring backbones and side chains.

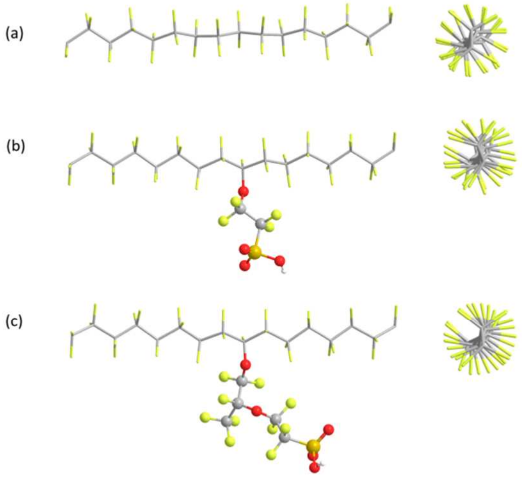


Fig.1. Optimized repeating unit structures of: (a) PTFE; (b) Aquivion; and (c) Nafion. The backbones exhibit a helical conformation involving rotation-reversal defects. The addition of side chains in Aquivion and Nafion has introduced some distortion to the backbones as seen on the right column.

In the present work, we performed first-principles based electronic structure calculations to simulate EEL spectra of PFSA membranes using the same method as we adopted in the previous study for PTFE systems.[24] The dielectric functions and ELNES were both calculated. The sampling of k-space in the Brillouin zone was performed by use of the Monkhorst-Pack scheme with maximum k-spacing of 0.07Å^{-1} for the ground state calculations and 0.04 Å^{-1} for the EELS calculations. The calculations were carried out with the GGA-PBEsol exchange-correlation functional.[25] A large number of empty bands were also included in the calculations to reproduce a converged plasmon peak in the low-loss spectrum. The polarization dependence of the optical response for helical PTFE chains was studied by varying the direction of the electric field vector of the incident electrons. Three components of the momentum transfer vector q in the [1 0 0], [0 1 0], and [0 0 1] directions were calculated and averaged to obtain low-loss spectra for polycrystalline systems. A Gaussian broadening of 0.15 eV was also included for the simulated spectra in the low-loss region. For core level spectra of carbon atoms, both instrumental smearing of 0.15 eV and lifetime broadening of 0.17 eV were considered in simulating the experimental spectra.

3 Results and Discussion

3.1 Experiment Results

Energy-loss spectra of PTFE, Nafion, and Aquivion in low- and high- loss regions were examined to understand the effects of the side chains on the conformation of the backbone. In the high energy loss region, similar shapes were observed in the fine structures of the carbon K-edge for the PFSAs and PTFE. As seen in Figures 2 (a-c), characteristic features in the range of 282-306 eV can be well fitted with a combination of six Gaussian and Lorentzian functions using the Quantifit program.[26] The details of fitting parameters of C-K ELNES are listed in Table 1. When compared to PTFE, the positions of all core-loss features are slightly altered for the PFSAs as shown in Figure 2 (d): an average of a +0.3 eV energy shift for Nafion and a –1.3 eV for Aquivion. Although other bonding states of carbon atoms (e.g., -C–O-) exist in the side chains, it is difficult to detect corresponding features from our experiments due to the weak signal of the side chains. Thus, the detectable differences of the C-K edge fine structures for PTFE and the PFSA membranes are primarily due to the conformational changes in the backbones due to the pendant side chains.

Table 1. Peak fitting parameters (in eV) of C-K ELNES for PTFE, Nafion, and Aquivion by Gaussian functions

	PTFE		**Nafion**		**Aquivion**	
Peak	**Position**	**FWHM**	**Position**	**FWHM**	**Position**	**FWHM**
a	287.02	1.30	287.45	1.11	286.08	1.20
*b**	289.11	1.03	289.31	0.82	287.93	0.69
c	292.17	2.54	292.89	4.44	290.52	4.20
d	294.51	1.71	294.95	1.69	293.46	1.70
e	297.24	2.23	297.58	3.03	296.25	6.30
f	299.58	6.74	300.54	6.36	301.86	9.11

* fitted with a Lorentzian function.

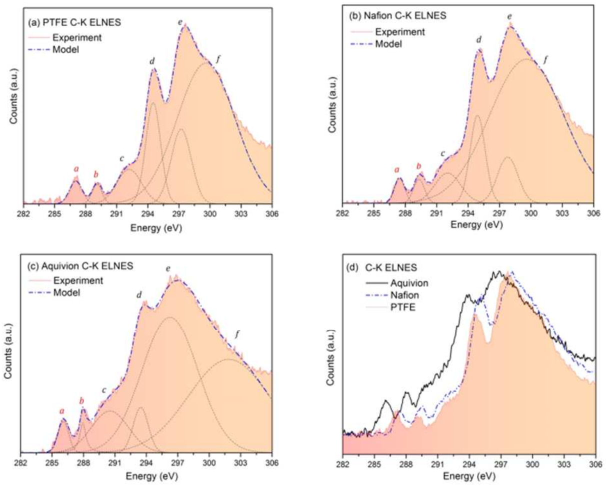


Fig.2. Quantitative analysis and fitting of C-K ELNES acquired in the STEM mode at room temperature: (a) PTFE; (b) Nafion; (c) Aquivion; and (d) comparison of the normalized spectra of the three materials. The single scattered profiles of carbon K-edge are generated after the removal of background (power-law function) and plural scattering (Fourier-ratio deconvolution) contributions.

In our previous EELS study of PTFE in different thermally dependent phases, we showed that the relative positions and intensities of the first two peaks (i.e., *a* and *b*) at the onset of the carbon K-edge are important features to distinguish chain conformations. The occurrence of these two peaks can be interpreted as the result of 1s→π* core level excitations that are related to the first two valence excitation peaks observed in the low-loss spectrum. As illustrated in Figures 1 (b-c), the pendant side chains in the PFSA ionomers tend to induce additional distortion to the backbones. This effect becomes even more evident for a PFSA with shorter side chains: randomly displaced CF_2 groups bring about extra conformational disorder on the backbone of Aquivion.

Comparison of the fitted peaks *a* and *b* in the range of 285–290 eV for PTFE and the PFSA ionomers reveals that the side chains alter the conformation of the backbones of both ionomers. The well-defined peaks *a* and b are separated by 2.1 eV in PTFE and 1.9 eV in the PFSA ionomers with minor differences in the shapes and intensities. The disordered backbones in the PFSA ionomers correspond to a slightly sharper peak *a* and *b*: the width of each peak is generally narrowed by 0.1 – 0.3 eV in the PFSA membranes when compared to PTFE. Unlike the other peaks which are well fitted with Gaussian functions in the core-loss region, the sharp maximum and long wings in peak *b* are fitted better with a Lorentzian function, which indicates it is closely related to an excitonic excitation that is possibly due to the adjacent CF_2 groups on the backbones.

We also computed the ratio of the integrated areas under peak *a* and peak *b* to estimate the concentration of disordered phases due to the conformational changes. For PTFE, peak *b* represents 52.8% of the total area under peaks *a* and *b*. This fraction is slightly lower for Nafion (i.e., 52.4 %) but significantly lower for Aquivion (i.e., 44.9 %). The relatively small peak *b* contribution for Aquivion is primarily due to the additional disorder of backbone due interaction of the short side chains. Although precise measurement of the concentration of disordered chains is not practical, studies of these characteristic peaks provides us an efficient way to evaluate the effects of side chains on the conformation of the backbones in PFSAs.

The features in the low-loss spectra are also examined in Figures 3 (a-c) by comparing the experimental results with computed spectra generated from a combination of multiple Gaussian and Lorentzian functions. In the spectrum for PTFE, a total of six peaks are easily resolved and fitted by these functions. All features in the same range are also repeated in the spectrum of Nafion while most of them are broadened and attenuated. For Aquivion, the signals from these features are significantly diminished. The step-wise features in the pre-plasmon region are no longer resolvable in the Aquivion membrane. Additionally, the characteristic peaks in the range of 5–10 eV are also expanded and cannot be distinguished easily as those appearing in PTFE and Nafion.

As shown in Figure 3 (d) and Table 2, the positions of peaks *a* and *b* in the spectrum for PTFE are nearly identical to those of Nafion. In contrast, they are all shifted approximately 1.3 eV lower in energy for Aquivion. For the three ionomers examined in this study, the energy difference between peak *a* and *b* remains 1.3–1.4 eV. By using the same approach as we have shown earlier for the C-K ELNES, the integration of areas under peak *a* and *b* were calculated. The relative intensities of peak *a* and *b* are related to the change in the concentration of disordered chain conformations in the different systems. The contribution of peak *a* to the total area of peak *a* and *b* has increased from 17.9 % for PTFE to 54.8 % for Nafion and 72.6 % for Aquivion.

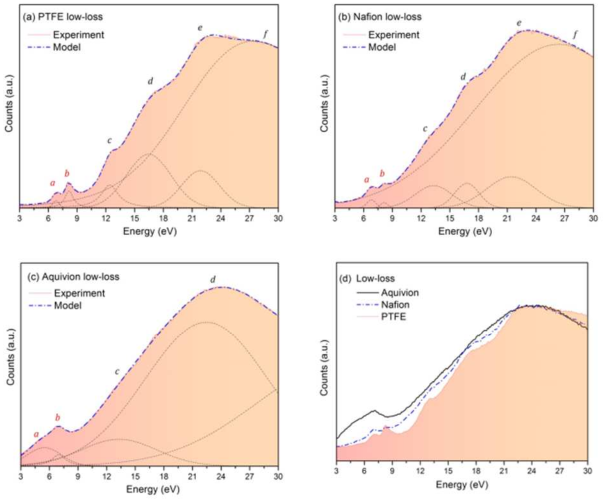


Fig.3. Quantitative analysis and fitting of the low-loss spectra acquired in the STEM mode at room temperature: (a) PTFE; (b) Nafion; (c) Aquivion; and (d) comparison of the normalized spectra of the three polymers. The spectra are collected in the energy-loss region of 0-30 eV followed by the removal of zero-loss (logarithmic function) and multiple scattering (Fourier-log deconvolution). The energy resolution of 0.15 eV is determined by the FWHM of the zero-loss peak.

Table 2. Peak fitting parameters (in eV) of low-loss spectra for PTFE, Nafion, and Aquivion by Gaussian functions

	PTFE		**Nafion**		**Aquivion**	
Peak	**Position**	**FWHM**	**Position**	**FWHM**	**Position**	**FWHM**
a	6.80	0.82	6.78	1.18	5.47	4.24
*b**	8.16	1.08	8.11	0.88	6.98	1.76
c	12.41	2.17	13.27	6.31	13.30	9.33
d	16.47	5.45	16.66	3.23	22.47	15.09
e	21.87	4.63	21.11	7.26	-	-
f	25.46	13.54	27.66	17.54	-	-

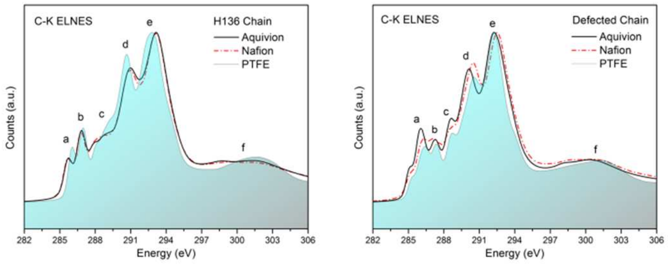
* fitted with a Lorentzian function.

3.2 Calculations of EELS

The experimental data reveal that most of the spectroscopic features observed in the low-loss and core-loss region in PTFE are also seen in Nafion and Aquivion. It was also observed that the shapes and intensities of the first two peaks at the onset of the carbon K-edge and the corresponding two peaks at the lower energy-loss region vary for the two ionomers. Clearly the chemistry of side chains and the backbone structure of the PFSA membranes can both affect the final spectra, and hence it is difficult to decouple their contributions using only experimental methods. Therefore, DFT calculations for Nafion and Aquivion with different PTFE backbone conformations were conducted to identify the specific spectroscopic features that are important in determining the chain conformations.

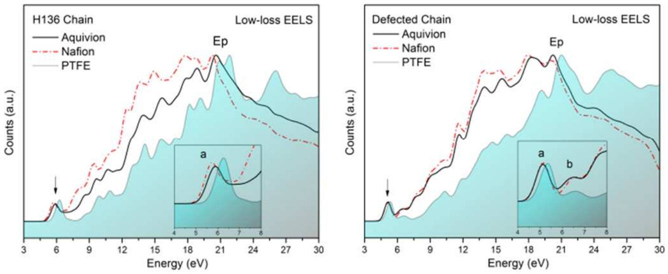
At room temperature, PTFE usually has two ordinary crystalline phases (i.e., H136 and H157) corresponding to two different helical conformations. In addition, a disordered phase involving a portion of H136 and H157 chains in reverse rotation is also present.[24] In our previous study of PTFE we showed that calculations based on this defected PTFE structure can successfully reproduce most of the spectroscopic properties seen experimentally. Hence, this structure was selected to construct PFSA backbones in the EELS calculations. To compare the effect of the different conformations on the final spectra, the H136 structure is also used.

The fine structures of the C-K spectra were calculated for the carbon atoms on backbones for PTFE, Nafion, and Aquivion and are displayed in Figure 4. A small energy shift of 0.4 eV for the PFSA ionomers is seen in Figures 4 (a) and (b). This energy shift is likely due to the change in local electron density of the carbon atoms on the backbones due to the tethered side chains. Very similar spectroscopic characters are observed in H136 and the defected systems. It should be noted that only the defected chain models can accurately predict the transition of the peaks (*a* and *b*) at the onset of the C-K edge for PTFE and the PFSA ionomers. As seen in Figure 4 (b), we also notice the presence of a shoulder near the onset of edge (~285 eV). This feature is not seen in the calculated spectra for H136 and the experiments. It may result from the additional disorder imposed by the defected chain in the PFSA ionomers. A careful comparison between the spectra shown in Figures 4(b) and 2(d), shows that the corresponding peaks can be identified from their relative positions. The ratio of the area under peaks *a* and *b* are nearly unchanged in Nafion and PTFE, while the contribution from peak *a* becomes more pronounced in Aquivion. This is consistent with the trend observed in the experiments.



(a) (b)

Fig.4. Calculated carbon K shell excitation spectra for PTFE, Nafion, and Aquivion based on different backbone conformations: (a) H136; and (b) defect.



(a) (b)

Fig.5. Calculated energy loss function (ELF) for PTFE, Nafion and Aquivion based on different backbone conformations: (a) H136 (b) Defected.

The calculated energy loss functions for PTFE and the PFSA ionomers based on different conformations are plotted in Figure 5. Similar gross features are observed in the calculations and in the experiments. The most intense peak in ELF in the region 3-30 eV is identified as the bulk plasmon peak (Ep) representing the oscillation of free electrons. For Nafion, the whole spectrum is generally shifted to lower energy by 0.5-0.7 eV. This energy shift is increased by 0.1-0.3 eV for the PFSA ionomer with short side chains (i.e., Aquivion) when compared to Nafion. Again, this is in good agreement with the trend we observed experimentally. It should be noted that the fine structures shown in the calculated low-loss EELS cannot be well resolved from the experiments due to the limitations of the instrument. The behavior of the inter-band transitions in the range of 4-8 eV is also examined. In both H136 and the defected systems, the dominant peak in this range is slightly shifted for the PFSA membranes (0.2-0.4 eV). The simulated spectra based on the defected backbones clearly show the presence of two peaks whose behavior is largely determined by the structure of the backbones. The intensities of the second peak increase due to the conformational changes induced by the side chains. Although the two peaks are well resolved in our calculations, the trend predicted from the results is different from that seen in the experimental low-loss spectra. This may be due to the effects of interchain interactions induced by the presence of the sulfonic acid groups on the side chains.

Comparison of the calculated spectra to the experimental EEL spectra in the low-loss and core-loss region indicates that the pendant side chains not only affect the chemistry of backbones but also induce a certain amount of distortion to the helical chains. These effects can be both verified in the EEL spectra and used as fingerprint information to distinguish different PFSA ionomers.

Conclusions

Two types of PFSA ionomers with distinct side chain chemistry (i.e., Nafion and Aquivion) were investigated by EELS in the low-loss and core-loss regions. Most of well resolved features in the EEL spectra of these ionomers are also seen in PTFE. The most unique spectroscopic features that distinguish the PFSA membranes from the PTFE are found on the onset of the C-K ELNES and the lower region in the valence EELS.

By comparing the fine structures of the C-K edge for the PFSA ionomers to the PTFE, we found that the spectra for both ionomers are shifted. The short side chain in Aquivion seems to have a greater influence on the final spectra. An energy shift of greater than 1 eV was observed for Aquivion in contrast to a shift of only 0.3 eV for Nafion. At the onset of the edge, the coupled peaks due to $1s \rightarrow \pi^*$ excitation are each fitted with a Gaussian or Lorentzian function. Further analysis revealed that the ratio of the integrated areas covered by these peaks is closely related to the backbone structures and thus can be used to distinguish the conformational properties of the PFSA ionomers. Again, Aquivion was seen to have the most distinctive ratio mostly due to the effect of the short side chains. The same trend was found in the calculated EELS. The results reveal that the energy shift is primarily due to the chemistry of the side chains while the change of peak ratio is the result of the structural changes of the helical chains.

In the low-loss EELS, characteristics of the bulk plasmon peak for a polymer are often used to study different phases.[19] As the PFSA ionomers have same backbone structure as PTFE, the shift in the plasmon peaks is most likely due to the changes in the helical conformations. As it is shown in low-loss spectra, PFSA with short side chain has the largest shift of plasmon peak which suggests a noticeable distortion on backbones. This is also confirmed from the calculated energy loss profiles. The behaviour of the two peaks in the range of 5-10 eV was also studied to characterize the conformational changes. Both peaks are sensitive to the structure of the backbone. The contribution from the second peak is increasingly suppressed as the side chain effects become more evident.

In summary, a comparative study of the spectroscopic properties of PTFE, Nafion, and Aquivion has shown that changes in the helical conformations of the backbones can be well characterized by use of a combination of experimental and theoretical EELS. Several characteristic features are identified as fingerprints for specific backbone conformations. This will allow one to further explore the structure-property relationships of PFSA ionomers by combining with other imaging techniques.

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Notes

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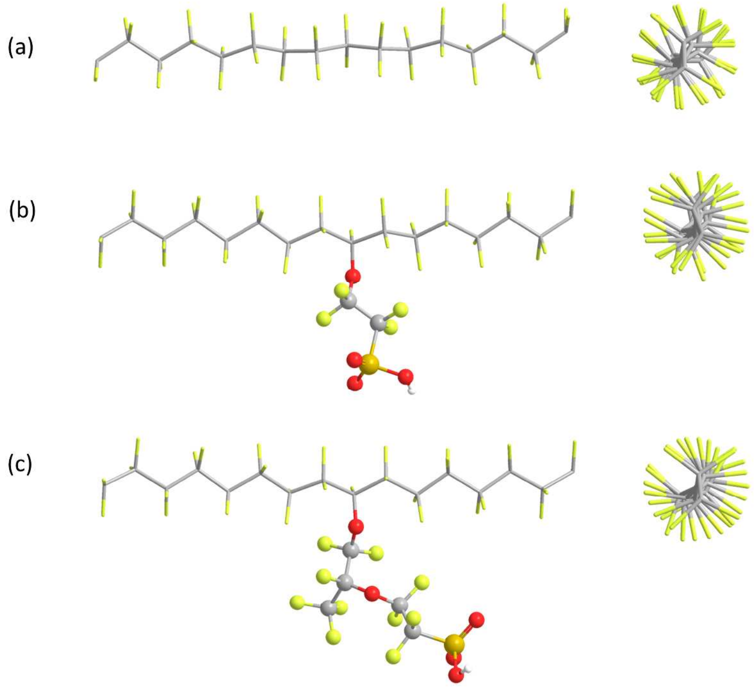
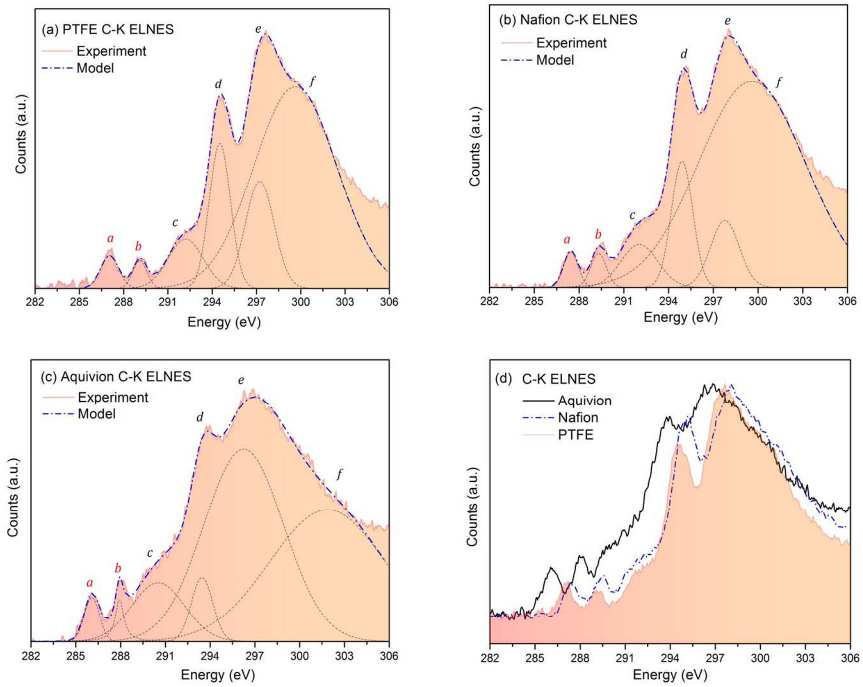
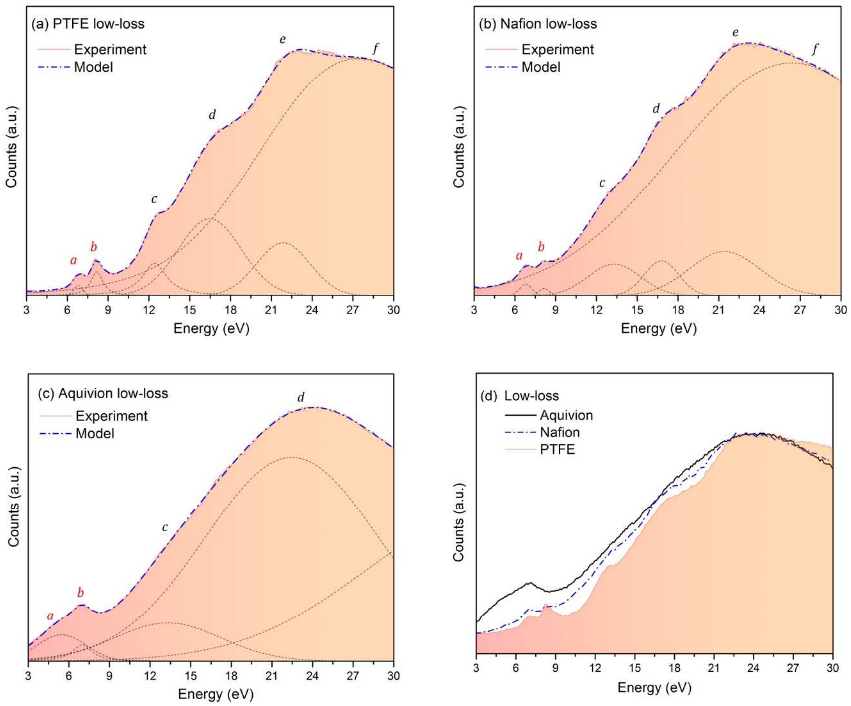
References

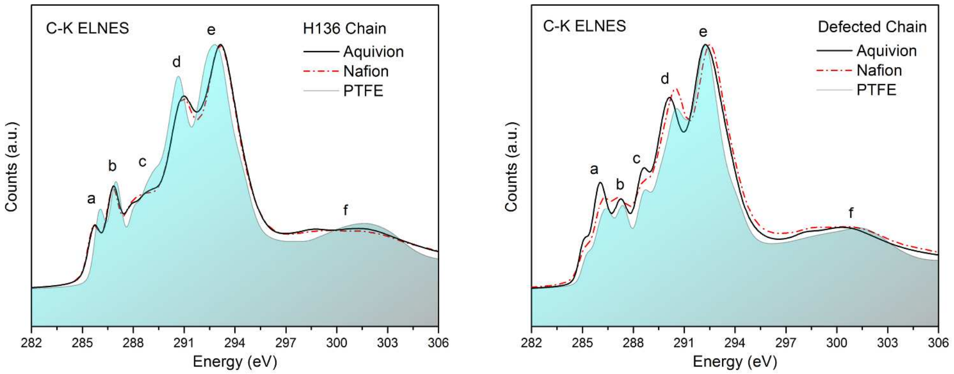
1 Y. Shao, G. Yin, Z. Wang and Y. Gao, *J. Power Sources*, 2007, **167**, 235-242.
2 B. Smitha, S. Sridhar and A. A. Khan, *J. Membr. Sci.*, 2005, **259**, 10-26.
3 R. Souzy and B. Ameduri, *Prog. Polym. Sci.*, 2005, **30**, 644-687.
4 K. Mauritz and R. Moore, *Chem. Rev.*, 2004, **104**, 4535-4586.
5 H. G. Haubold, T. Vad, H. Jungbluth and P. Hiller, *Electrochim. Acta*, 2001, **46**, 1559-1563.
6 A.-L. Rollet, G. Gebel, J.-P. Simonin and P. Turq, *J. Polym. Sci., Part B: Polym. Phys.*, 2001, **39**, 548-558.
7 T. Xue, J. S. Trent and K. Osseo-Asare, *J. Membr. Sci.*, 1989, **45**, 261-271.
8 C. Wang, V. Krishnan, D. Wu, R. Bledsoe, S. J. Paddison and G. Duscher, *J. Mater. Chem. A*, 2013, **1**, 938-944.
9 J. T. Wescott, Y. Qi, L. Subramanian and T. Weston Capehart, *J. Chem. Phys.*, 2006, **124**, 134702.
10 J. A. Elliott, D. Wu, S. J. Paddison and R. B. Moore, *Soft Matter*, 2011, **7**, 6820-6827.
11 G. Dorenbos and K. Morohoshi, *J. Mater. Chem.*, 2011, **21**, 13503-13515.
12 S. J. Paddison and J. A. Elliott, *Solid State Ionics*, 2006, **177**, 2385-2390.
13 K. D. Kreuer, M. Schuster, B. Obliers, O. Diat, U. Traub, A. Fuchs, U. Klock, S. J. Paddison and J. Maier, *J. Power Sources*, 2008, **178**, 499-509.
14 M. J. Hannon, F. J. Boerio and J. L. Koenig, *J. Chem. Phys.*, 1969, **50**, 2829-2836.
15 H. A. Willis, M. E. A. Cudby, G. W. Chantry, E. A. Nicol and J. W. Fleming, *Polymer*, 1975, **16**, 74-76.
16 A. Gruger, A. Régis, T. Schmatko and P. Colomban, *Vib. Spectrosc.*, 2001, **26**, 215-225.
17 K. Varlot, J. M. Martin and C. Quet, *Micron*, 2000, **32**, 371-378.
18 J. J. Ritsko and R. W. Bigelow, *J. Chem. Phys.*, 1978, **69**, 4162-4170.
19 M. R. Libera and R. F. Egerton, *Polym. Rev.*, 2010, **50**, 321-339.
20 O. Dhez, H. Ade and S. G. Urquhart, *J. Electron Spectrosc. Relat. Phenom.*, 2003, **128**, 85-96.

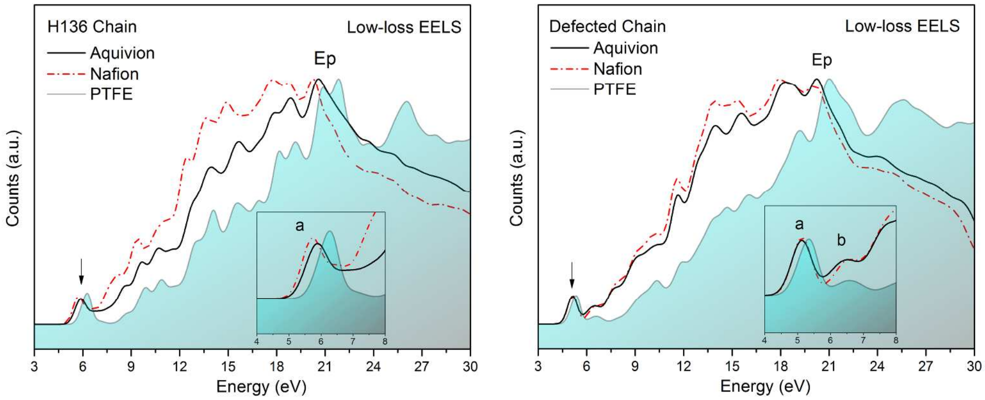
21 A. P. Hitchcock, J. J. Dynes, G. Johansson, J. Wang and G. Botton, *Micron*, 2008, **39**, 311-319.
22 V. J. Keast, *Mater. Charact.*, 2012, **73**, 1-7.
23 P. Rez and D. A. Muller, *Annu. Rev. Mater. Res.*, 2008, **38**, 535-558.
24 C. Wang, G. Duscher and S. J. Paddison, *Microscopy*, 2014, **63**, 73-83.
25 J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, **100**, 136406.
26 G. Duscher, M. E. Hmielewski and J. D. O. Oduor, *Microsc. Microanal.*, 2009, **15**, 446-447.


(a)
(b)
(c)


(a) PTFE C-K ELNES
Experiment
Model
a
b
c
d
e
f
Counts (a.u.)
282
285
288
291
294
297
300
303
306
Energy (eV)
(b) Nafion C-K ELNES
Experiment
Model
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)
(c) Aquivion C-K ELNES
Experiment
Model
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)
(d) C-K ELNES
Aquivion
Nafion
PTFE
Counts (a.u.)
Energy (eV)


(a) PTFE low-loss
Experiment
Model
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)
3
6
9
12
15
18
21
24
27
30
(b) Nafion low-loss
Experiment
Model
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)
(c) Aquivion low-loss
Experiment
Model
a
b
c
d
Counts (a.u.)
Energy (eV)
(d) Low-loss
Aquivion
Nafion
PTFE
Counts (a.u.)
Energy (eV)


C-K ELNES
H136 Chain
Aquivion
Nafion
PTFE
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)
282
285
288
291
294
297
300
303
306
C-K ELNES
Defected Chain
Aquivion
Nafion
PTFE
a
b
c
d
e
f
Counts (a.u.)
Energy (eV)


H136 Chain
Low-loss EELS
Aquivion
Nafion
PTFE
Ep
a
Counts (a.u.)
3
6
9
12
15
18
21
24
27
30
Energy (eV)
4
5
6
7
8
Defected Chain
Low-loss EELS
Aquivion
Nafion
PTFE
Ep
a
b
Counts (a.u.)
3
6
9
12
15
18
21
24
27
30
Energy (eV)
4
5
6
7
8

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Characterization of Chain Conformations in Perfluorosulfonic Acid Membranes using Electron Energy Loss Spectroscopy

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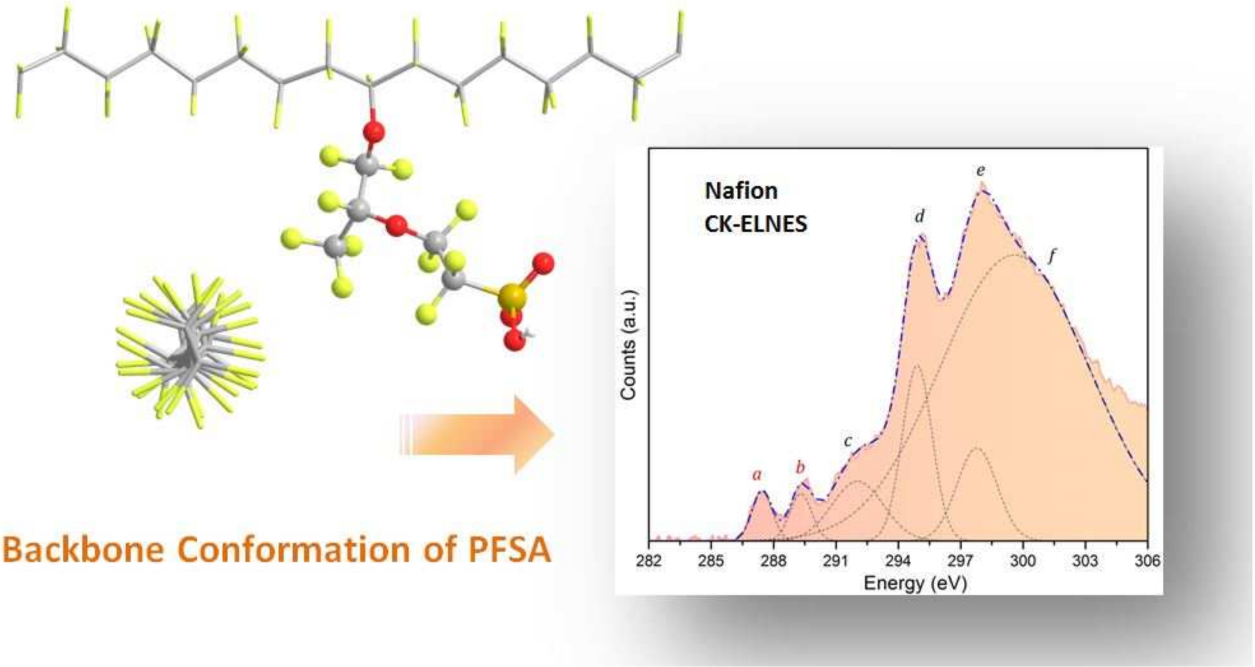

The side chain effects on the PTFE backbone conformation in the family of perfluorosulfonic acid ionomers were first investigated with electron energy-loss spectroscopy and first principles calculations.