# Computational modelling and structural studies of perfluorosulfonate ionomer membranes

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## ABSTRACT

Perfluorosulfonate ionomer membranes (PIMs) consist of a polytetrafluoroethylene, or "Teflon", backbone with sulfonic acid groups periodically substituted along the chain, and are of great commercial interest due to their peculiar ion transport properties. In particular, under certain conditions, these membranes are selectively conductive, passing cations preferentially to anions. This makes them ideal as efficient membrane separators in redox fuel cells. It has been known for some time that the interesting properties of PIMs derive from the microscopic phase separation of hydrated ionic material and the fluorocarbon matrix. However the precise nature of this remains controversial.

In this paper, we present data from small angle X-ray scattering (SAXS) and molecular dynamics studies which provide convincing evidence that PIMs possess an ion-clustered morphology with a structural hierarchy. In particular, a model-independent instantiation of the segregation between polar and non-polar material can be obtained from a maximum entropy interpretation of the SAXS data. Such models are consistent with surface images of membranes taken with atomic force microscopy, and molecular dynamics simulations show that these structures demonstrate selective conductivity in the presence of an applied electric field.

**Keywords**: perfluorosulfonate ionomer membranes, X-ray diffraction, maximum entropy, molecular dynamics, fuel cells

## 1 INTRODUCTION

### 1.1 Perfluorosulfonate ionomers

"Nafion", a contraction of sodium (Na) fluorinated ionomer, is the trade name of the first ionomer containing sulfonate groups to be synthesized on a commercial scale. This was achieved by researchers at E. I. du Pont de Nemours and Company during the mid-1960s, and made feasible by the development of a free radical copolymerization process which circumvented the problem of spontaneous side-polymerizations which affected antecedent techniques. Since then, a number of other perfluorosulfonate ionomers, which are chemically very similar to Nafion, have been manufactured by the Asahi Chemical Company (under the trade name "Aciplex") and the Asahi Glass Company (under the trade name "Flemion"). The Dow Chemical company have also produced a perfluorosulfonate ionomer, which differs from Nafion by virtue of its shorter ionic side-group.

The advantages of sulfonate ionomers over varieties which contain carboxylate groups are principally due to the greater polarity of the sulfonic acid group. They are also more resistant to pollution by divalent cations in solution. The combination of a stable fluorinated backbone and the highly polar sulfonate group make Nafion, and membranes similar to it, extremely important materials. This is principally due to their selective conductivity, favoring the passage of cations over anions—an inorganic analogue of passive transport through a cell membrane. By investigating the structural nature of phase separation in perfluorosulfonate ionomers, it was hoped that the mechanism of this selective conductivity would become clear.

### 1.2 SAXS from perfluorosulfonate ionomers

In the early 1980s, a series of papers were published describing the small-angle X-ray scattering (SAXS) from PIMs [1]–[6] that results from the electron density contrast between the fluorocarbon matrix and hydrated ionic material in the membrane. The two dimensional data showed a broad maximum with an equivalent Bragg spacing of between 35–55 Å [2] that was attributed to ionic aggregation, and is commonly referred to as the 'cluster' reflection in subsequent studies. The 'cluster' reflection became more intense and moved to smaller angles on hydration. This was taken to imply that the ionic aggregates in the membrane were swelling, and becoming increasingly less dense with respect to the fluorocarbon matrix. The reflection also moved to lower angles and higher intensity as the equivalent weight (EW), or the mass of dry membrane per mole of ion exchange groups, was decreased. The interpretation of this was that the increased concentration of ionic groups caused a corresponding increase in aggregate size, and a drop in density relative to the matrix. There was little change in the position of the reflection on ion exchange with monovalent cations, including lithium, sodium and potas-

sium, but the intensity decreased dramatically as cation size increased [4], [5]. It was thought that this effect is mainly related to the hydrophobicity of the cation, which affects the equilibrium water content of the membrane. However, the electron density of the cation is also a factor.

Also present in the data, but initially receiving rather less attention, was an upturn in scattering at very low angles, which has been explained variously as being due to beam divergence, large scale density fluctuations [2], chain-folded fluorocarbon lamellae [5] or higher order ionic agglomerates [7], [8]. However, systematic intensity variations in this feature with membrane water content have been observed, which indicates that it likely to have the same origin as the 'cluster' reflection. More recently, an ultra-small angle scattering study was conducted in the range 0.3–0.0003 Å$^{-1}$ [9]. This revealed the existence of large-scale fluctuations with a correlation length of greater than 3000 Å. In summary, there is a substantial body of evidence to support the existence of macroscopic structure, *i.e.* on a scale above the 'cluster' level, but the precise nature of this organization is not yet well understood. In this paper, we will attempt to construct a coherent picture of the morphology of perfluorinated ionomer membranes from the molecular to the mesoscopic level.

## 2 SAXS AND MAXIMUM ENTROPY

The main difficulty with interpreting the SAXS from PIMs is that there are many different possible structural models that are consistent with the scattering data. In particular, the issue of whether the 'cluster' reflection is of intra- or interparticle origin, *i.e.* whether the scattering is produced by individual ionic aggregates (*e.g.* the core-shell model of MacKnight [10]) or by interference between ion-clustered domains (*e.g.* the infinite paracrystalline model due to Marx *et al.* [11]), remains somewhat controversial. Clearly, a model-independent method for interpreting the scattering data is highly desirable for systems such as PIMs which possess such a low degree of spatial order.

One such technique, developed by the current author, is based on a maximum entropy reconstruction of the charge density distributions giving rise to the observed SAXS. The method is described more fully elsewhere [12], but can be summarized very briefly as follows. If we have a discrete real space charge distribution with elements $\rho_i$, then the resulting X-ray diffraction intensities $F_j$ are defined by the product of a structure factor $R$ and its complex conjugate:

$$F_j = R_j R_j^*  \tag{1}$$

where the structure factor $R_j$ is defined by the discrete Fourier transform of $\rho_i$:

$$R_j \equiv \sum_i^N \rho_i \exp\left(\frac{2\pi I i j}{N}\right).  \tag{2}$$

The convention $I \equiv \sqrt{-1}$ is used to avoid confusion with the suffix $i$.

Although the charge distribution $\rho_j$ is given by the inverse discrete Fourier transform of $R_i$, shown in equation (3), the crucial difficulty is that $\rho_j$ is mathematically indeterminate for a particular set of diffraction intensities $F_j$.

$$\rho_j \equiv \frac{1}{N} \sum_i^N R_i \exp\left(\frac{-2\pi I i j}{N}\right)  \tag{3}$$

That is to say, given an experimental X-ray diffraction pattern we do not have enough information to reconstruct a corresponding charge density uniquely. This is often referred to as the 'phase problem' by crystallographers, and quite severely restricts our ability to draw conclusions about systems with low degrees of spatial order as the diffraction data are too poor to adequately constrain the system. In order to carry out the reconstruction, some additional assumptions must be made. What assumptions can be made without unduly biasing the final structure towards a particular model?

If we define the Shannon entropy of charge distribution:

$$S \equiv -\sum_i^N \rho_i \left\{\log\left(\frac{\rho_i}{DEF}\right) - 1\right\},  \tag{4}$$

where $DEF$ is a parameter calculated from the total charge,

$$DEF \equiv \exp\left(\frac{\sum_i^N \rho_i \log \rho_i}{\sum_i^N \rho_i}\right)  \tag{5}$$

then by maximizing equation (4) with the constraint that the chi-squared fit between the simulated diffraction pattern $F_i$ and some experimental data $D_i$ containing standard errors $\sigma_i$, given by equation (6), be as small as possible we can find the most probable charge distribution consistent with the observed scattering data. Essentially, the MaxEnt procedure works by maximizing the uncertainty in the unknown degrees of freedom subject to macroscopic constraints on the system. In fact, although the problem is trivial to set up, the actual maximization procedure is rather involved and interested readers are referred to the original paper [12], which describes a modified version of a method developed by Skilling and Gull [13].

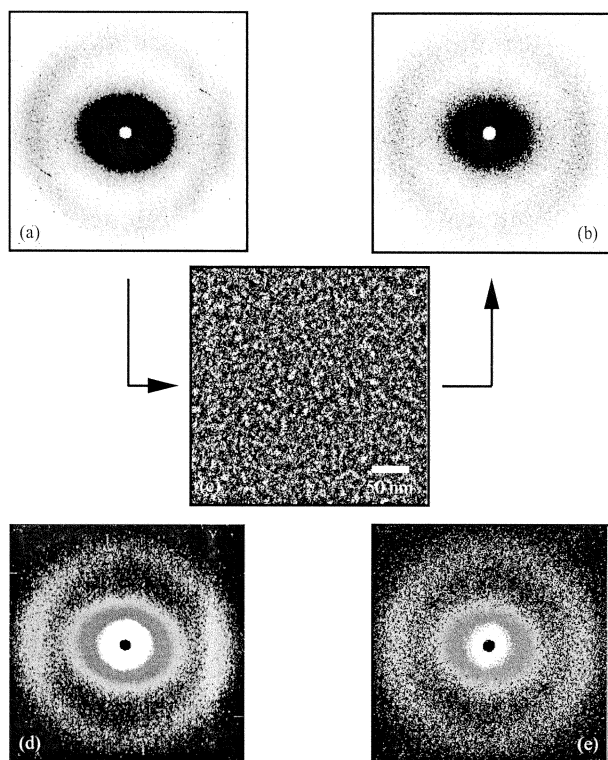$$C \equiv \sum_i^N \frac{(F_i - D_i)^2}{\sigma_i^2}  \tag{6}$$

Figure 1: MaxEnt reconstructions of SAXS data from Nafion 115 $H^+$ membrane with extrusion direction vertical: (a) experimental data, (b) simulated diffraction pattern of MaxEnt charge distribution, (c) MaxEnt charge distribution after 590 iterations of algorithm, (d) gamma enhanced experimental data and (e) gamma enhanced MaxEnt diffraction pattern.



Figure 2: Comparison of (a) low pass filtered MaxEnt reconstruction with (b) AFM phase image of Nafion 115 $H^+$ membrane under ambient conditions. Both images have been gamma enhanced to emphasize areas of low electron density and high hydrophilicity, respectively.

The results of this procedure applied to SAXS patterns obtained from a Nafion 115 (1100 EW, 5 thou $\simeq 127\mu m$ thick) membrane in the acidic ($H^+$ cation) form at ambient temperature and humidity are shown in Figure 1. Two dimensional, point collimated SAXS data were collected using nickel-filtered Cu $K\alpha$ radiation on a flat plate Rigaku-Denki camera, with a typical sample-to-film distance of around 25 cm. The X-ray generator was an Elliott GX21 rotating anode. The diffraction patterns were digitized and corrected for Lorentz-polarization effects and sample absorption.

The original data, which were the sole input to the MaxEnt algorithm, are shown in Figure 1a. The reconstruction is shown in Figure 1c, and its diffraction pattern is shown in Figure 1b. Figures 1d and e are versions of 1a and b, respectively, in which the greyscale palette has been manipulated to emphasize the 'cluster' reflection in each of the two patterns. The original data, Figure 1a, and the diffraction pattern of the reconstruction, Figure 1b, compare well by visual inspection. This is borne out by a reduced chi-squared value of 1.41. Furthermore, an internal test parameter pro-
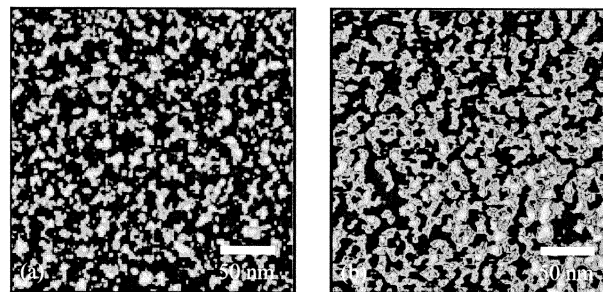
duced by the algorithm indicates that it is a very good approximation to a MaxEnt image.

It therefore follows that the MaxEnt reconstruction must contain features which give rise to the 'cluster' reflection and the low angle upturn (discussed in the introduction), both of which display signs of orientation. However, it is not immediately clear from Figure 1c what these features are. In order to make sense of the reconstruction, the spatial components need to be separated using Fourier transform methods. This work is described in detail elsewhere [14], and will be discussed during the conference presentation, but Figure 2 shows a comparison between a low-pass filtered MaxEnt reconstruction and a phase contrast image obtained from the surface of the membrane by atomic force microscopy (AFM) [15]. The hydrophilic regions in the membrane correspond to areas that are rich in water, which also give rise to SAXS due to their relatively low density compared to the fluorocarbon matrix. Thus, the logical interpretation of the low angle upturn is that it is produced by agglomerates of ionic clusters. Although the MaxEnt structure need not necessarily correspond to the thermodynamically optimal structure, we will now show that such ion-clustered morphologies also emerge naturally from atomistic simulation.

## 3 MOLECULAR DYNAMICS RESULTS

Although classical molecular dynamics (MD) is intrinsically unable to deal with the size of model considered in the previous section, we have shown in work described elsewhere [16] that it is capable of reproducing smaller scale ion-clustered morphologies which are consistent with those determined from SAXS and AFM, and that demonstrate selective conductivity of cations and anions. We only have space to briefly summarize this work here.

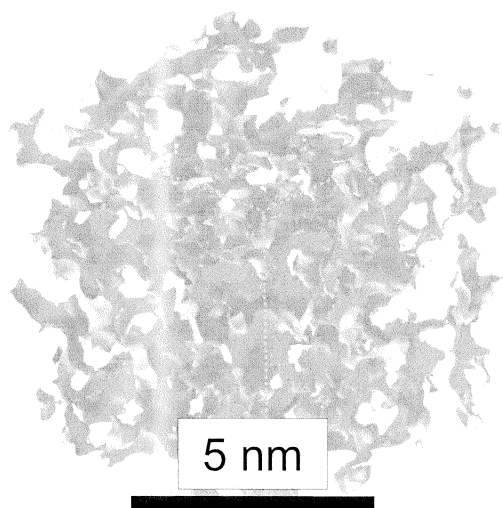The models were constructed by simulating mixtures

**5 nm**

Figure 3: Three-dimensional Connolly surface produced from an MD simulation of 15.9% by mass TIP3P water molecules, plus ionic fragments including sulfonic acid groups, hydroxonium ions and hydroxyl ions. To generate the surface, all non-membrane components were deleted leaving a network of sulfonate fragments (hidden for clarity) bordered by a surface shaded by proximity to the polar regions of the matrix. In this case, darker regions are more polar lighter regions.

of ionic fragments of the Nafion polymer mixed with water, hydroxonium and hydroxyl ions. After several hundred picoseconds of constant NVT dynamics, the components were found to rearrange to form a phase separated morphology as shown in Figure 3. Figure 3 is a Connolly surface produced from an equilibrated model containing 15.9% water by mass by removing all water molecules and visualizing the interfacial surface bordering the hydrated ionic material and the fluorocarbon matrix.

The resulting network of channels is shaded darker in regions where the surface is close to polar (negatively charged) sulfonic acid moieties and lighter where is it close to relatively non-polar fluorocarbon material. During the simulations, positively charged ionic species (*i.e.* hydroxoniums) were found to hop between negatively charged darker regions, whilst negatively charged species (*i.e.* hydroxyls) were confined to the bulk water phase. The net result was that, in the presence of an applied electrical field, the mobility of the hydroxonium ions was found to be over three times greater than the hydroxyl ions despite the much greater size of the former. Switching off the electrostatic interactions resulted in a reversal of this trend, with mobility being simply related to ionic size.

Although the preceding atomistic models are quite naïve in that they oversimplify the component of a real membrane, give cluster sizes smaller than those observed experimentally and neglect proton transfer or any quantum effects, they nevertheless demonstrate a similar jump-diffusion behaviour predicted by Hsu and Gierke using their phenomenological cluster-network model [17]. As computational resources become ever more powerful, it is increasingly possible to refine the atomistic models in order to obtain semi-quantitative predictions of resistivities, selectivities and electro-osmotic drag coefficients for use in process modelling.

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