



EXCHANGE VISIT GRANT: SCIENTIFIC REPORT

Reference Number : 4238

Title of the proposed research project : Multiscale modeling of Morphologies and Proton transport in hydrated Hyflon Ion H membranes for fuel cells.

Date of visit (starting date) : 08/05/2013

Duration : 12 week(s)

Applicant's Name : Dr. Luana De Lorenzo, Rende (CS), Italy

Host Institute: Soft Matter Chemistry Group, Leiden University, The Netherlands

1) Purpose of the visit

Proton-exchange membrane fuel cells (PEMFCs) have been widely explored in the last four decades. Perfluorosulfonic acid (PFSA) membranes consist of a highly hydrophobic polytetrafluoroethylene (PTFE) backbone with perfluorinated ether side chain (SFVE) terminated by hydrophilic $-\text{SO}_3\text{H}$ group, leading to spontaneous phase segregation at the nanostructural level, especially in solvent.

The short-side-chain (SSC) PFSA membrane, originally synthesized by Dow Chemical and now commercialized by Solvay Solexis as Hyflon [1] showed proton superconductivity and enhanced performance in fuel cell, higher crystallinity and glass transition temperature when compared to Nafion, the archetypal of PEMFCs, a long-side-chain (LSC) PFSA membrane (Scheme 1) [2]. Wide-angle, Small-angle X-ray (WAXS and SAXS) and neutron scattering technologies (SANS) have been widely utilized to probe the hydrated morphology of PFSA membranes [3].

Detailed knowledge of the morphology could be exploited for improving the PEM performance for fuel cell applications, since the ionomer morphology determines the network connectivity of the membrane and influences its conductivity and mechanical performance [4].

After the first visit during which I started to analyze the phase behavior inside Hyflon ion H by means of dynamic density functional theory (DDFT) [5] with Flory-Huggins mixing parameter χ calculated by means of fully atomistic approach [6], I go on in refining the DDFT simulations of PFSA membranes in order to obtain an acceptable agreement between calculated and experimental scattering curve and to better describe the morphology and physical properties of these materials. An accurate model for estimating the exact monomeric composition inside Hyflon ion copolymers has been developed: chemical structure, polymer microstructure, sequence distribution, and morphology of acid-bearing polymers are important factors in the design of polymer electrolyte membranes (PEMs) for fuel cells. The formation, dimensions and connectivity of ionic pathways are consistently found to play an important role in determining the physicochemical properties of PEMs and their performance in fuel cell applications.

In order to carry out this project I need to deepen my first acquaintance in mesoscale and macroscale modelling and to practice with the computational advanced codes developed in the host group for achieving the goal of validating the morphologies of hydrated Hyflon Ion H membranes. The research line of Multiscale Computational Chemistry in the Soft Matter Chemistry Group at Leiden University is interested in the fundamentals of multiscaled computational chemistry for bridging the quantum, molecular, mesoscopic and macroscopic scales. In this group a novel computational platform CULGI [7] has been developed: it is an international company for providing industry with modeling tools for the rational design of formulations, comprising polymers, colloids, surfactants and actives. Culgi

employs computational scientists, physical chemists, and software engineers. The staff of Soft Matter Chemistry Group develops and distributes the Culgi multiscale modeling library, and offers scientific support and consulting through an international network of application scientists.

The purpose of the exchange visit is to collaborate directly with this renowned research group, in order to gain my scientific knowledge in this field, to learn how using the program that they designed and finally to acquire skills, through on-site training, for developing new modeling approaches to investigate innovative and complex nanostructured functional materials.

2) Description of the work carried out during the visit

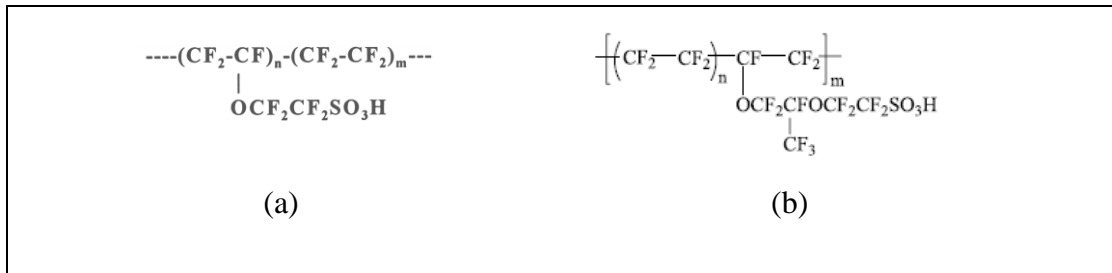
The phase behavior inside Hyflon ion H and Nafion membranes has been investigated by means of dynamic density functional theory (DDFT)[5]. The block copolymer film has been modeled as a collection of Gaussian chains, each representing a copolymer molecule in a mean field environment. The chain has been built from coarse-grained statistical units (beads) with composition $\{B_xS_2\}_m$ where A bead types denote the PTFE units of the apolar backbone and S_2 the polar side chains; x has been varied from 5 to 11 to capture different EWs of 635, 803, 909, 1076 g/eq. The chain of Nafion with EW of 1100 g/eq has been modeled as $\{B_8S_3\}_m$. Because experimental data is lacking the required mean-field Flory-Huggins mixing parameter χ has been estimated from the Hildebrand solubility values of the constituent materials of each bead by means of fully atomistic approach [6].

Molecular dynamic simulations of the mixed systems and their pure components have been carried out to calculate these values. Taking these bead interaction parameters DDFT runs have been performed. All the calculations have been performed by running scripts generated with Culgi 7.0. The morphologies of the Hyflon Ion H membranes (Scheme 1) have been investigated by varying the equivalent weight (EW) and water content (ϕ_w).

Crystallites are important components of the structure of perfluoropolymers membranes. They are crucial for mechanical properties, acting as physical crosslinks. The crystallinity of Nafion at 1100 equivalent weight has been estimated to range between 5 and 20%, based mostly on wide-angle X-ray diffraction [8]: the crystallinity content of these materials is due to the high percentage of apolar Teflon backbone chain and we have to take into account the crystalline domain for matching experimental scattering curve that present a peak at small q due to the crystallites: from SANS study the shape of those is elongated and approximately cylindrical [9].

During this visit we focus on the importance of the microstructure—here we use the classical description referring to the arrangement of monomer units along a polymer chain—and morphology of the constituent acid-bearing polymers on the properties of PEMs. However, going back on the original literature of the synthesis of these polymers, one readily found that the effect on the chemical composition is already known from the monomeric distributions along the chain. This phenomena has been related by the patent literature to batch polymerization which results in a relevant drift in chemical compositions. Experimental reactivity ratios have been used [11] in the present investigation and the batch polymerization processing results in a huge drift of compositions. Unfortunately the exact composition of these materials is not known, no data has been surprisingly reported in the extensive experimental literature, so we have to speculate about the effect of estimated monomeric compositions on morphologies and ionic conductivity. The most important finding of the research done during the visit is the strong heterodispersity found in these materials resulting from the batch

processing: thus implies a high percentage of backbone polymer densely packed and only 15-20 %wt of ionic side groups.



Scheme 1: Structures of: (a) Hyflon ion H; (b) Nafion repeat unit.

3) Description of the main results obtained

Molecular dynamic simulations of the mixed systems and their pure components have been carried out to calculate these values. The systems have to be relaxed for 30 ps at 600 K, and the system has to be compressed to the desired density at a rate of 0.1 Å/ fs while the temperature was annealed from 600 to 300 K at a cooling ratio of 50 K/1 ps, where the desired density was the bulk densities of TFE, SFVE, Hyflon Ion H and water.

Taking these bead interaction parameters DDFT runs have been performed. All the calculations have been performed by running scripts generated with Culgi 7.0 on the cluster provided by the group.

We performed first series of DDFT simulations on 3D models 64h*64h*64h (h= grid spacing) including only the amorphous copolymers of Hyflon ion H and Nafion at different water composition. The equilibrated structures are considered as a function of EW and degree of hydration. In particular the 2D snapshots of water density fields are shown in Figure 1 for four different systems of Hyflon Ion: (a) EW=635, x=5, m=5, φw=40%; (b) EW=635, x=5, m=5, φw=60%; (c) EW=803, x=6, m=5, φw=40%; (d) EW=909, x=7, m=5, φw=30%.

For the two systems with the lowest EW, an increase of the water content from φw= 40 to 60 % gives rise to a transition of elongated water clusters to a continuous water matrix domain with polymer micelles. Both the systems (c) and (d) shows bi continuous water clusters with increasing pore sizes

The three components of diffusion coefficient (D_x , D_y , D_z) on the equilibrated mesoscopic simulation boxes have been calculated by CG porosity Calculator tool of the software Culgi [7]. The algorithm is based on solving a Poisson equation for an inhomogeneous system with space dependent local field f and scalar potential P :

$$\nabla \cdot f \nabla P = 0$$

The porosity is a measure for the openness of an inhomogeneous system, which is characterized by the effective diffusion coefficient of an ideal test particle. We found very similar values for all the three

components of diffusivity: this is typical of bi-continuous and isotropic phased structures with no orientation in any direction, thus leading to a homogeneous flux of permeant across the simulated models.

WAXD scattering analysis have been performed on equilibrated 3D simulation boxes of 128h*128h*128h for the series of copolymers Hyflon ion H with the same ϕ_w values of Gebel et al [2]; the plots are showed in Figure 2. The calculated scattering curves are in good agreement with the experimental data for high q while for small q the crystallinity has to be taken into account.

Due to the lack of experimental data, a detailed study of the synthesis of the most known commercial perfluoropolymer's membranes for fuel cell applications (Nafion, Hyflon Ion H, Dow, Aciplex) has been performed and a copolymerization model of PFSI systems based on experimental reactivity ratios of the two monomers [11] has been developed: we observed an huge composition drift due to the higher reactivity of PTFE monomer compared with that of SFVE monomer. An accurate study on the synthesis condition of the most known commercial PEM perfluoropolymers lead us to treat these copolymers as phase-separated mixtures of long crystalline backbones chain and short copolymer chains. Further and more refined DDFT simulations of larger 3D models 128h*128h*128h (h = grid spacing) have been performed introducing a mixture of crystalline PTFE long chain B_{100} (p_C) and short gaussian chains of Hyflon ion H $\{B_xS_2\}_m$ (p_{COP}) at different water uptakes. We set $\chi_{p_C/p_{COP}}=0$ assuming a phase separated mixture and a relative composition in weight $p_C:p_{COP}=3:1$; we set $\chi_{S/W}$ (polar side chain beads /water beads) = -1: the water molecules across PEM membranes have shown to be carried by the polar groups so we set a strong interaction between the corresponding beads in our model. The snapshots of the Hyflon ion H with EW=808 g/eq and water compositions of 20-30-40 %wt has showed in Figure 3: the systems show bi-continuous elongated channels of water uniformly spread inside the volume of simulation boxes, that become highly interconnected at increasing water contents. By performing the scattering analysis on the equilibrated structures (Figure 4) we found a good agreement with the experimental curves (dependence q^{-1}) also for small value of q [2]. The scattering maximum located at large q values ($q_{max} \approx 0.15 \text{ \AA}^{-1}$) corresponds to the well-known "ionomer peak" while the scattering maximum located at low q values can be attributed to a crystalline component related to the long period between the lamellar crystallites [3]. The existence of crystallinity in the EW= 808 g/eq SPC polymer was previously evidenced by both WAXD scattering and differential scanning calorimetry (DSC) experiments. Since Nafion membranes do not exhibit crystallinity for EW values lower than 1000 (as observed by WAXD), the existence of a well-defined crystalline component in the small-angle scattering curve for the EW = 808 g/eq SPC PFSI confirms the higher level of crystallinity observed by reducing the pendant side chain length. This behavior was attributed to the fact that the shorter pendant side chains disrupt to a lesser extent the crystalline arrangement of the PTFE segments [10]. Thus, in agreement with the previous study on these ionomers, it is apparent that the higher crystallinity index observed for SPC PFSI is indication that the copolymerization is not statistical, such that a significant fraction of long run length PTFE segments exists in the polymer microstructure.

A satisfactory agreement between calculated curves of Figure 4 and experimental SANS profiles of EW= 808 Hyflon Ion reported by Gebel et al. lead us to conclude that the proposed model well represents the microstructures and the morphologies of SSC PEMs and also the networks of elongated (with an almost cylinder shape) of water channels visible from the showed snapshots (Figure 3) is in agreement with experimental findings.

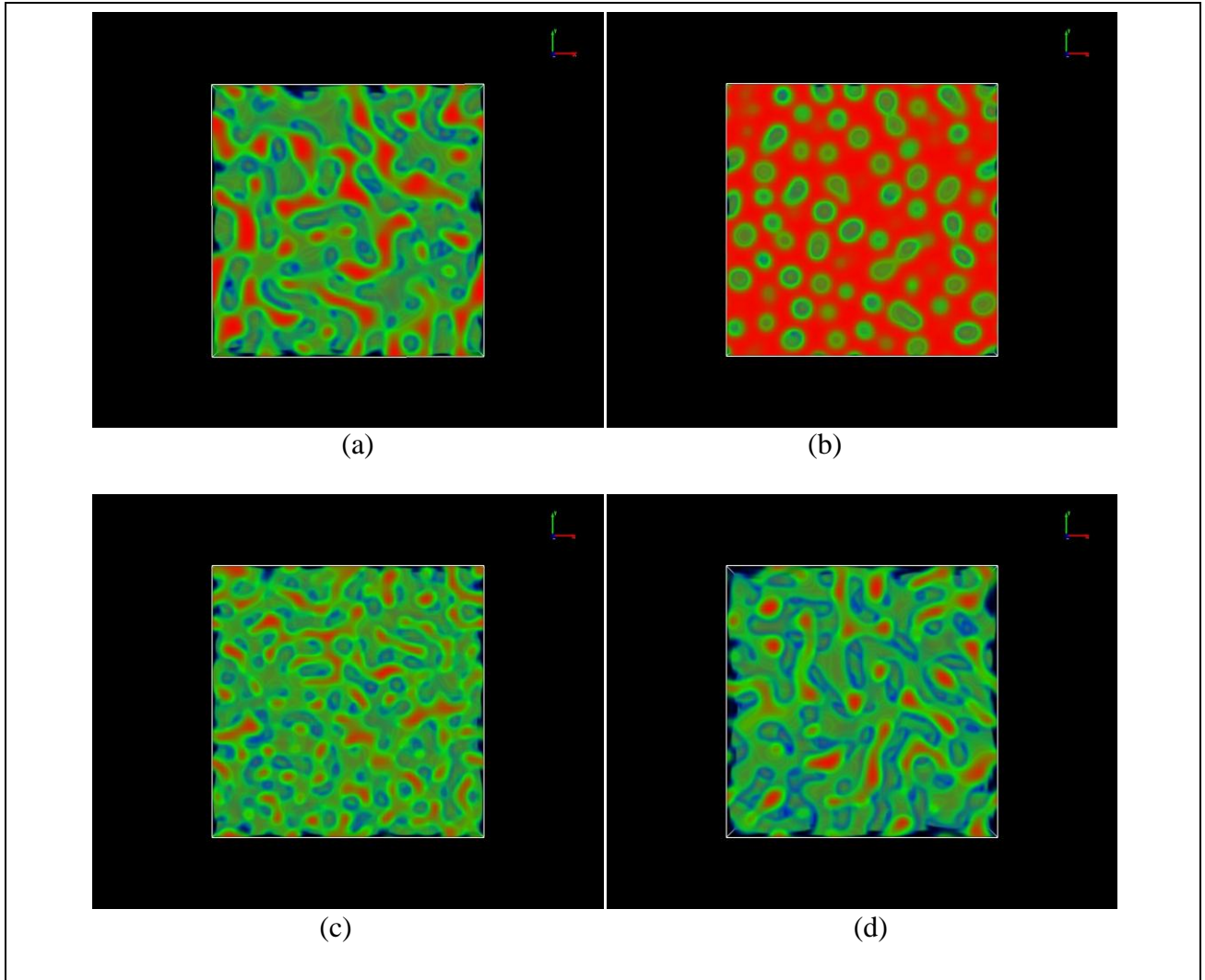


Figure 1: Snapshots of the density fields of water as a 2D cross section from 3D models $64h \times 64h \times 64h$ ($h =$ grid spacing) of the hydrated Hyflon ion H membranes with (a) $EW=635$, $x=5$, $m=5$, $\phi_w=40\%$; (b) $EW=635$, $x=5$, $m=5$, $\phi_w=60\%$ (c) $EW=803$, $x=6$, $m=5$, $\phi_w=40\%$; (d) $EW = 909$, $x=7$, $m=5$, $\phi_w=30\%$.

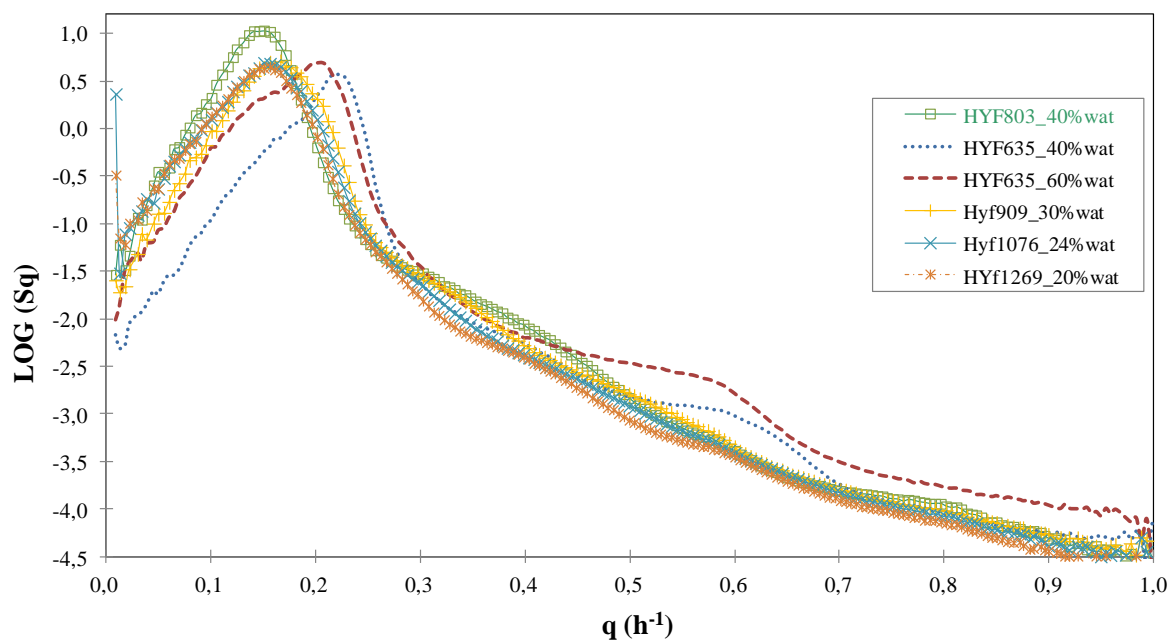


Figure 2: Simulated small-angle scattering curves for simulated models of Hyflon ion H systems at different water content.

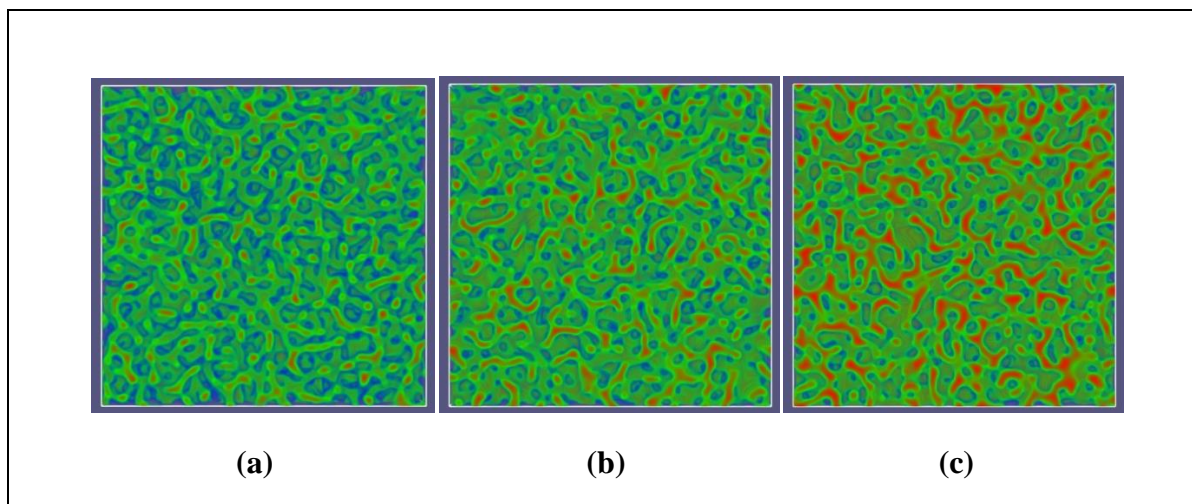


Figure 3: Snapshots of the density fields of water as a 2D cross section from 3D models $128h \times 128h \times 128h$ (h = grid spacing) of the hydrated Hyflon ion H membranes of $EW=803$, $x=5$, $m=5$, with (a) $\phi_w = 20\%$; (b) $\phi_w = 30\%$; (c) $\phi_w = 40\%$.

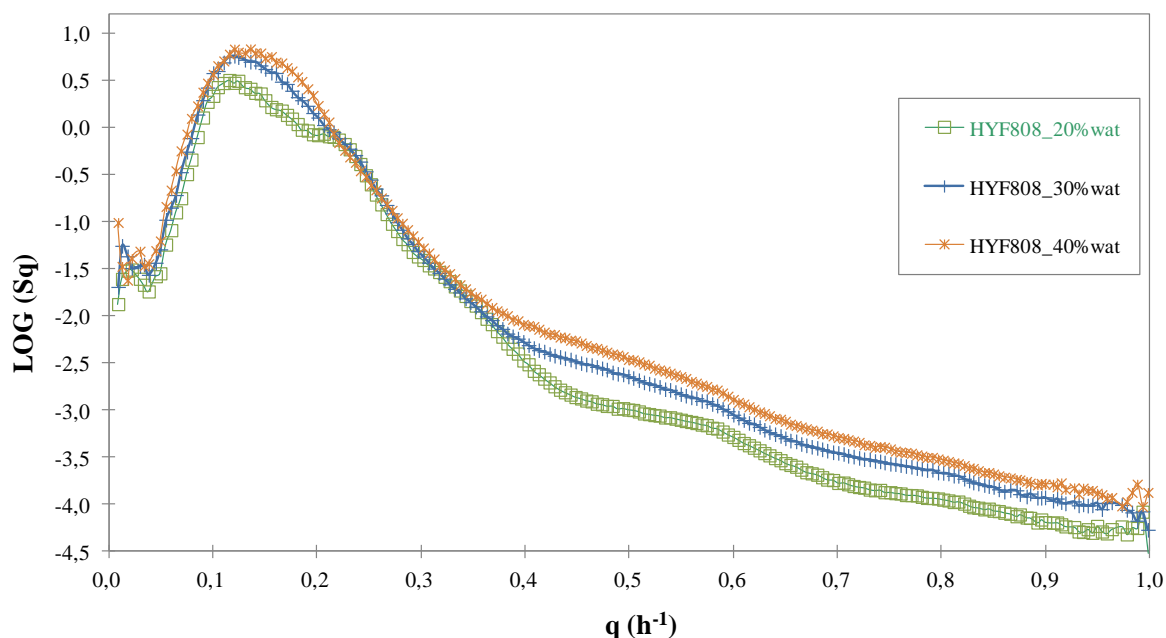


Figure 4: Simulated small-angle scattering curves for simulated models of Hyflon ion H copolymers of EW=808 at 20-30-40 % wt content of water.

References

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4) Future collaboration with host institution (if applicable)

In this second visit I better investigated the intricate microstructure of perfluorocopolymers membranes for fuel cell. We match theoretical results with experimental data of WAXD and SAXS profiles on these membranes by assuming a phase separated composition of long crystalline backbone with short copolymers chain and ensuring that the water molecules are driven in the matrix by the polar side groups (negative χ parameter)[2]. A modeling approach based on a polymer monomeric distribution

calculated by batch processing and experimental reactivity ratios has been developed and validated in order to better represent the morphology of these materials.

I'm happy with the obtained results and I really would like to collaborate in future with SMC group of Leiden University mainly for achieving two goals:

- 1) To model proton transport across the validated structures,
- 2) To build up a systematic procedure of mapping from fully atomistic to coarse grained models in order to link the two modeling techniques.

5) Projected publications / articles resulting or to result from the grant (ESF must be acknowledged in publications resulting from the grantee's work in relation with the grant)

Mesoscale Modeling of Morphologies in hydrated Hyflon Ion H membranes for fuel cells.

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6) Other Comments (if any)

I felt very comfortable during the exchange visit in such a collaborative and stimulating scientific group as the Soft Matter Chemistry Group of Leiden University.

I acknowledge the ESF Committee for giving me the grant for the second longer visit in the chosen host institute and the opportunity to enlarge my knowledge, to get better results and to improve my skills on mesoscale modelling by "on site" training in this stimulating and renowned host group.