Insights into Interfacial Water Structuring at the Nafion Surface by T1-Weighted Magnetic Resonance Imaging

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ABSTRACT

T_1-weighted Magnetic Resonance images of water in the surroundings of a Nafion surface allowed to identify the presence of a Low Mobility Zone (LMZ), 60 μm thick, consisting of water molecules structured in a hydrogen bonding network, promoted by the presence of the acidic protons on the surface of the sulphonated polymer. In parallel, the Exclusion Zone (EZ) was assessed by observing in optical microscopy the distribution of microspheres suspended in the medium in contact with the Nafion membrane. It was found that the LMZ and the EZ do not

correspond: in fact, the former is thinner and more stable over time than the latter and they behave differently when ions are present in the medium in which Nafion is immersed.

INTRODUCTION

Phenomena at the interface between water and different types of surfaces continue to raise interest for their relevance both in biological and in chemical processes. It is generally accepted that surfaces (either biological ones, such as those made of proteins or cellular/organellar membranes, and inorganic surfaces, such as colloids) are surrounded by several hydration layers, which are considered to have a role on the establishment of interactions with approaching ions, molecules or nano-sized particles. In this view, macromolecules, colloids or membranes' components must overcome these forces to come into contact with each other or with solutes and suspended materials. In this context, it is still controversial whether these repulsive forces are due to the occurrence of a long-range water structuration in the hydration layers or to other mechanisms.[1]

In the last two decades, much attention has been devoted to the study of a phenomenon known as Exclusion Zone (EZ). The phenomenon deals with the observation that different types of colloidal particles (e.g. microspheres with various functional groups on their surfaces) and a variety of macromolecular solutes (e.g. proteins and dyes) are extensively excluded from a region adjacent to hydrophilic surfaces, such as those provided by hydrophilic polymers, hydrogels or ion-exchange beads. The exclusion zone is reported to extend up to hundreds of micrometers from the surface and its thickness varies upon the type of surface, the excluded

molecules and the experimental conditions.[2-5] Different hypotheses about the nature of the forces that cause the exclusion have been proposed. According to a first hypothesis, EZ may originate from electrostatic attractive/repulsive forces between (partially) charged surfaces and molecules.[6,7] However, this hypothesis is not convincing, as both negatively and positively charged microspheres at the interface with the same surfaces experience the exclusionary force.[4] EZ could instead be reliably explained as a chemotactic phenomenon at the water-surface interface. Microspheres in this zone behave as macromolecules in a gradient of co-solutes and experience a thermodynamic force which pushes them to move up or down along the gradient depending on the type of interaction existing between co-solutes and the macromolecules themselves.[8,9] Finally, G.H. Pollack and co-workers proposed that the exclusion zone is the result of the extension in space of the surfaces ordering effect on water molecules. The authors reported UV, NMR and IR data supporting the theory of a thick, structured layer of water molecules endowed with lower mobility and diffusivity with respect to bulk water.[3]

Aim of this work is to exploit Magnetic Resonance Imaging (MRI) to investigate the characteristics of water in the EZ in order to get more insight into the mechanisms that are at the basis of the exclusion phenomenon. In T_1 and T_2 weighted MR images, water signal should be affected first of all by the mobility of water molecules, as a more constrained cluster of water molecules is expected to provide a signal that is different from that of the "bulk" water. Such an effect has indeed been observed by Pollack and co-workers in a T_2 map of water in contact with a polyvinyl alcohol (PVA) gel, where a darker area, 60 μm thick, adjacent to the gel surface, was detected. Its T_2 value was slightly lower than that of bulk and interstitial water, suggesting a lower mobility of water in that region. The same authors also reported pulsed field gradient spin-echo diffusion measurements on the same specimen, indicating the presence of an interfacial

region in which water diffusion was substantially different from either the bulk water or gel phases.[3] Nevertheless, no quantitative data were given.

In the present work, the mobility of water molecules in the surrounding of hydrophilic surfaces has been evaluated by the acquisition of T_1-weighted MR images. Under extreme narrowing conditions T_1 is inversely proportional to the molecular reorientational time (τ_R), and regions in which the motion of water molecules is limited should appear as brighter areas in the corresponding T_1-weighted images, affording new information about the nature and extension of the exclusion zone. Measurements were performed on a Nafion membrane, as this sulfonated tetrafluoroethylene copolymer[10] has been reported as one of the best materials able to induce thick and stable EZs.[11,12]

Samples were also imaged by optical microscopy in the presence of a suspension of polystyrene or polycarboxylated microspheres (used as tracers of the EZ). The data obtained by the two imaging techniques were compared in order to seek for a correlation between the presence of the EZ, visible at the optical microscope, and the structuring of interfacial-water, detectable in MR T_1-weighted images.

EXPERIMENTAL SECTION

Nafion membranes (N1110 - 254 μm thick -, N117 - 183 μm thick -, and N115 - 127 μm thick, as 0.30x0.30m sheets) were purchased by Ion Power GmbH (Terminalstraße Mitte 18, 85356 München). Cleaning of the membranes was carried out by repeated washings in HNO_3 1M at

100°C and in EDTA 0.01M at room temperature. Upon comparing MR images and T_1 values no appreciable differences were found between cleaned and untreated specimens.

Nafion membranes were hydrated in water for at least 24 hours before every experiment.

All chemicals were obtained from commercial sources and used without further purification.

MRI

All MRI experiments were acquired at room temperature at 7 T on a Bruker Avance 300MHz spectrometer equipped with a microimaging probe. Hydrated membranes were fixed on a rigid inert support prior to immersion in the given solution. In most cases a cuvette was used (see figure 1a). Samples were positioned inside the MR Imager with the membranes aligned along the direction of frequency encoding in order to avoid chemical shift artefacts. Images were obtained using a standard T_1-weighted multislice spin echo sequence (TR/TE/NEX = 900ms/13.5ms/60; FOV 2.8cm; one slice, 1mm, in-plane resolution 27x27μm; total acquisition time 14 hours); T_1 measurements were performed using a multislice spin echo sequence with variable repetition time. Temperature was controlled and fixed at 298K during all MR experiments.

OPTICAL MICROSCOPY

A Leica DM IRB optical inverted microscope (magnification x100) was used for optical microscopy imaging investigations. Hydrated membranes were immersed in the desired solutions and a suspension of Polybead polystyrene microspheres (diameter 1μm), either non functionalized

(neutral) or carboxylated (negatively charged), was added (microspheres concentration in the resulting dispersion: 0.005% w/v). Both types of microspheres were purchased by Polysciences Inc (Hirschberg an der Bergstrasse, Germany).

Observations were carried out immediately after samples preparation, 1h, 4h and 24 h later, at room temperature ($296 < T < 299K$). No temperature control was used. Reported values of EZ thickness are averages of three different preparations.

RESULTS AND DISCUSSION

Figure 1b shows a T_1-weighted MR image of a PolyEthylene Therephtalate Glycol (PETG) sample and a Nafion membrane N115 both immersed in bi-distilled water. PETG is not permeable to water and it does not affect surrounding water at all. On the contrary, water soaks into Nafion pores and as a result the membrane appears as a bright rectangle in the ^1H image. In fact, interstitial water generates an hyperintense signal due its limited mobility inside the Nafion pores. A region characterized by an intermediate signal intensity, about 60 μm thick, is clearly detected at the interface between the membrane and the bulk water. This finding suggests that water mobility in this area is intermediate between that of bulk and interstitial water.

To get more insight into the differences associated to the changes in water mobility, longitudinal relaxation times of bulk, interstitial and interfacial water were measured. Obtained values are the following: T_1 bulk water = 3.4 ± 0.3 s; T_1 interfacial water = 1.7 ± 0.2 s; T_1 interstitial water = 0.25 ± 0.03 s. The short relaxation time of interstitial water suggests that its mobility is markedly affected by the confinement inside the Nafion pores. The intermediate relaxation time of interfacial water suggests that water in this zone is neither as restrained as interstitial water nor as free as bulk water. Its lower mobility could be associated to the presence

of a network of hydrogen bonds that could lead to an enhanced water structuring. In this work, we will refer to this area as Low Mobility Zone (LMZ).

The possibility that the reduction of T_1 in this area is due to some field inhomeogeneity at the interface between bulk water and the polymer can be ruled out because this type of effect (already small since there are no paramagnetic substances in the sample able to cause great dishomogeneity) is canceled by using a spin echo sequence, as done in this work.

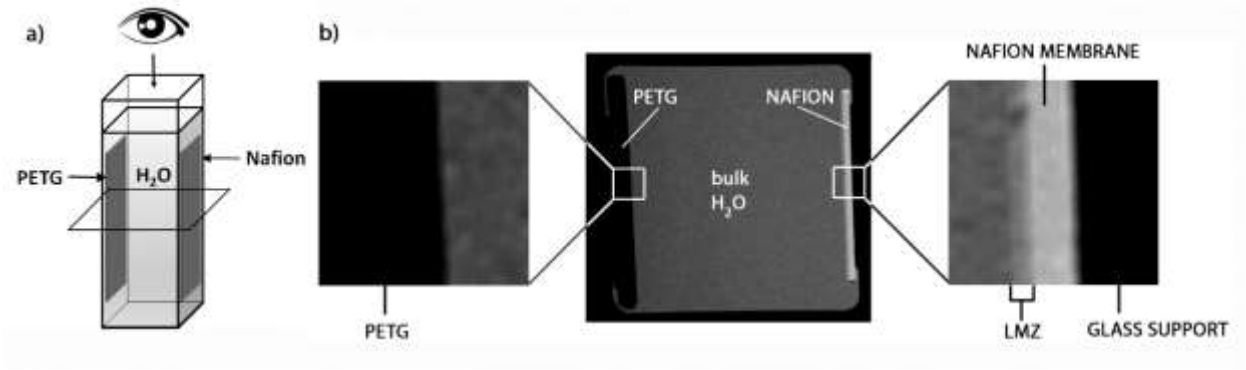

FIGURE 1: a) schematic representation of the phantom used for the acquisition of MR images: PETG and Nafion samples are fixed on the walls of a cuvette filled with water; b) T_1-weighted image of water protons in the presence of N115 (on the right) and PETG (on the left), axial projection. The LMZ is visible on the Nafion surface but not on PETG.

To ensure that the brighter zone adjacent to the Nafion surface is not due to the progressive swelling of N115 in water, images of N115 were also acquired after 24 hours of hydration in order to allow the membrane to be completely hydrated, obtaining the same result.

LMZ thickness does not appear to be dependent on the thickness of the Nafion membrane, as two other types of membrane (183 μm -N117- and 254 μm -N1110- thick, respectively) yield the same LMZ. In the following, data obtained by using the N1110 membrane will be presented.

Furthermore, the LMZ does not change with time, as demonstrated by repeating MRI acquisitions after 24 hours.

Figure 2 shows the image obtained at the inverted optical microscope when a N1110 Nafion membrane is immersed in an aqueous suspension of polycarboxylated polystyrene microspheres. These particles have been used to assess the occurrence of the EZ in previous work.[2-4] The EZ (defined as the region where the particles are excluded) extends, on average, up to about 160 μm immediately after sample preparation. Its extension appears to be strongly time dependent: in fact, it drops down to about 40 μm after 4 hours and vanishes after 24 hours. Analogous results (data within the error reported in table 1) were obtained using not functionalized, not electrically charged microspheres. It can be noticed that a partial negative charge is also present on the surface of not functionalized microspheres, due to residual surface sulfate ester groups leftover from synthesis with sulfate based surfactants and initiators, as reported on the related Polysciences datasheets. Nevertheless, the same residual charge is also present on carboxylated microspheres, and the size of the observed EZ is quite similar in the two cases in spite of different net surface charges. The observed behavior demonstrates that the EZ cannot be associated to electrostatic attractive/repulsive forces between the charged Nafion surface and the residual electric charge on the particles.

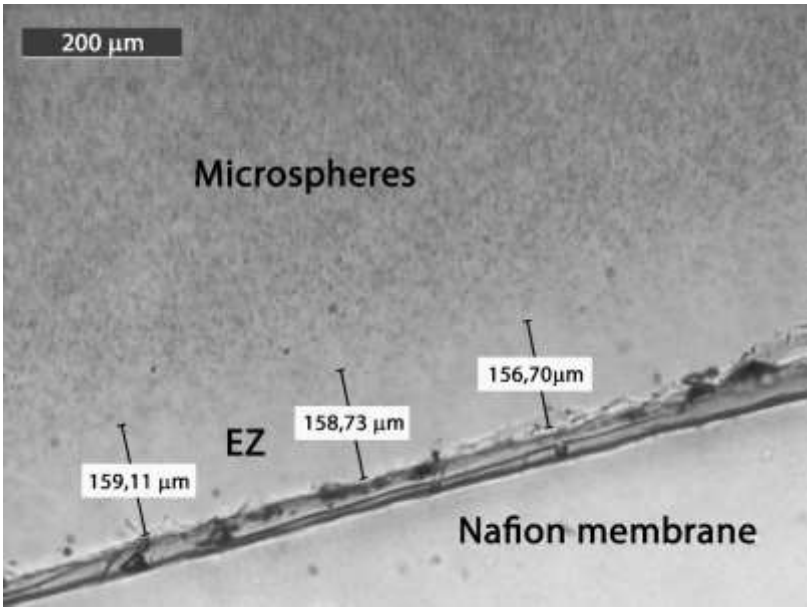

FIGURE 2: Polystyrene microspheres exclusion from the N1110 surface as observed at the inverted microscope immediately after sample preparation (magnification 100x). Nafion surface appears irregular and less transparent along the cutting line.

Conversely from what was observed for the LMZ, the EZ thickness appears to be directly proportional to membrane thickness: in fact it was assessed to be 120 µm for N117 and 70 µm for N115 respectively, when measured immediately after sample preparation.

INFLUENCE OF pH AND SALTS ON EZ AND LMZ

Even if the presence of a layer of structured water at the Nafion surface has been demonstrated, its size, as well as the non-dependency on Nafion membrane thickness and the stability with time, makes it different from what is usually recognized to be the EZ in the

proximity of the polymer surface. In fact, the LMZ appears thinner, independent of membrane thickness, and stable on time.

These findings appear to be in contrast with the view that the structuring of water molecules at the interface with hydrophilic polymers is responsible for the exclusion of chemicals and particles from the region adjacent to the polymers' surface. At least, it seems that this cannot be the only mechanism determining the exclusion phenomenon. In fact, in MR images only the contribution from the more structured water molecules is detectable, whereas the large EZ extension observed at the optical microscope could be the result of more than one phenomenon and it is not possible to isolate one contribution from another.

In order to get further insight into the relationship between LMZ and EZ, MR images were acquired in different conditions of pH and salts concentrations and the results were compared with those obtained in optical microscopy for the exclusion of microspheres under the same conditions. The obtained results are shown in Table 1.

It must be noticed here that initially all the negatively charged sulphonic groups on the Nafion membrane have protons as counterions, as a consequence of the equilibration with strong acid performed by the manufacturer and further pre-treatment of Nafion with HNO_3. These protons are released in the medium after immersion of the membrane, causing acidification, which takes place over few minutes. The final overall pH, as measured by a standard pHmeter, is reported in a separate column. When the contact medium is represented by a basic solution, these surface-associated protons are neutralized at a different extent depending on the solution pH. Hence, other counterions replace them. Ion exchange also takes place when the contact solution contains salts.

		EZ μm			LMZ μm (±15 μm)
	Final pH	**t_0**	**t_1**	**t_2**	
H_2O	4.2	140±15	77,3±13	39±4	60
Buffer $NaHCO_3/Na_2CO_3$ 10mM pH10	8.2	101±11	111±17	102±11	30
Buffer KH_2PO_4/K_2HPO_4 10mM pH8	6.9	103±4	0	0	30
Buffer H_3PO_4/KH_2PO_4 10mM pH2	1.3	87±14	85±7	0	60
HNO_3 10mM pH2	1.3	0	0	0	60
$NaNO_3$ 10mM		108±10	0	0	60
HCl 10mM pH2	1.3	0	0	0	60
NaOH 10mM pH12	9.6	167±11	119±14	116±9	0
NaCl 10^{-3}mM		164±15	132±16	97±13	60
NaCl 10mM		102±7	50±11	0	30
NaCl 30mM		85±11	0	0	30

TABLE 1. Thickness of EZ and LMZ in media with pH and salts concentration. Polystyrene microspheres were used as tracers for the assessment of the exclusion zone immediately after the preparation of the sample (t_0), after 1h (t_1) and after 4h (t_2). A great variability is observed in the determination of EZ as even minimal changes in the experimental conditions (i.e. room temperature) and the tendency of microspheres to form aggregates dramatically affect the measurement.

In general, data shown in table 1 suggest that at increasing salts concentration both EZ and LMZ thickness decrease (see NaCl 0.01, 10 and 30mM), in accordance with previously reported

data,[4] until vanishing when all the protons on the membrane surface are replaced by Na^+. No relevant differences among different salts are evident (compare, for example, NaCl, phosphate buffer and $NaNO_3$ at neutral pH and at the same concentration at $t_{0,}$), in spite of the different diffusive and water-structuring characteristics of the ions (diffusion coefficients for the involved ions range between $0.69x10^{-9}$ m^2s^{-1} for HPO_4^{2-} and $2.03x10^{-9}$ m^2s^{-1} for Cl^-,[13] and their water structuring capability is also different according to their positions in the Hofmeister series[14]). A strong, opposite pH effect is observed on the EZ and the LMZ respectively in the presence of pure acids or bases: acidic pH (e.g. HCl and HNO_3) quenches the exclusion while leaving the LMZ unchanged; conversely, basic pH (NaOH) increases EZ thickness and stability while the LMZ disappears. In buffered solutions (e.g. phosphate buffer pH=2), both salt and pH effect are present and their effects cannot be independently assessed; accordingly, intermediate situations are observed.

T_1 in the LMZ does not appear to be influenced by the chemical composition of the medium as it remains constant around the above reported value (1.7 s).

The reported data clearly support the view that the EZ and the LMZ are not representations of the same phenomenon, and cannot be accounted for on the basis of the same physical principles.

It can be reasonably stated that the LMZ is generated by the structuring effect of a strongly polarized polymeric surface on adjacent water molecules, as demonstrated by the higher longitudinal relaxation rate of water protons in this region. The presence of H^+ as counterions on the surface and at the interface with bulk water seems to be a key point for the observed decreased water mobility. In fact, when the Nafion sample is immersed in a basic solution, H^+ neutralization and replacement by Na^+ or other cations occur, with the concomitant

disappearance of the LMZ. The same effect, although at a lesser extent, is observed in the presence of salts, where only H^+ replacement by cations (and not neutralization) takes place. This can be explained on the basis of the strong structuring power of protons at the interface between Nafion surface and water, which are able to bind and orientate water molecules via strong hydrogen bonds. As their number decreases, the hydrogen bonding network loses its strength and extends to a lower distance from the surface. It is interesting to note that it is not necessary to exchange/neutralize all the surface/interface protons to completely quench the LMZ (e.g. with the NaOH concentration used here only about one half of the Nafion sulphonic sites are actually exchanged). The presence of other ionic species in solution could also disturb the order in the structured water layer by interposing and diffusing among water molecules, thus contributing to the reduction of the LMZ thickness.

On the other side, as far as the EZ is concerned, our results appear to be in agreement with the views of Schurr et al, who suggested that the exclusion phenomenon is generated by the movement of charged microspheres into pH gradients at the interface between Nafion and water,[10] and by Florea *et al.*, who described the exclusion of non-functionalized polystyrene microspheres on the basis of a combination of ion exchange at the interface, diffusion of ions, and diffusiophoresis of colloids in the resulting ion concentration gradients.[15] According to Schurr's suggestion, in the presence of NaOH (medium pH higher than surface/interface pH), in spite and independently of the disruption of the LMZ, an outwards force acts on the negatively charged microspheres keeping them distant from the surface, and a thick and stable EZ is observed. Conversely, acidic mediums cause an inwards flux in the generated pH gradient (no exclusion), while the LMZ is present because it is not affected by pH gradients. When neutral microspheres are used the total electrolyte gradients can be considered, according to Florea's

hypotesis. In this case, in the presence of NaOH an outwards concentration gradient is present due to consumption of exchanged Na^+ ions on the Nafion surface; this causes ions in solution to diffuse inwards and hence particles to be "pushed" away from the surface. In HCl, no exchange takes place and the particles are not subjected to any ion flux on their surfaces, and are thus free to approach the surface.

In both cases, once the pH or ion concentration gradients are canceled, the chemotactic forces are canceled too and normal diffusion takes place, thus causing the EZ to quickly decrease with time.

Phosphate buffer at pH 2 represents an intermediate situation: pH would cancel the exclusion, but the presence of K^+ ions partially balances the effect, and an intermediate EZ size is observed.

The partial negative surface charge due to residual surfactant anions in non–functionalized microspheres, as well as the neutralization of the negative charge on polycarboxylated microspheres at acidic pH, also play a role in the establishment of the exclusion phenomenon, as the motion of particles in ion gradients is affected by their surface electric charge.

The LMZ is not affected by the gradients, as it is determined by protons present on the polymer surface and at the interface with bulk water, and it does not involve any other molecule/particle which could be subjected to chemotactic or diffusiophoretic forces.

CONCLUSIONS

The MRI measurements suffer for a relatively low resolution and do not allow to distinguish effects that induce changes in the LMZ smaller than 30μm (voxel size). The actual LMZ extension could be slightly different with respect to that reported herein (30 or 60 μm). In fact, it is reasonable to assume that the farer are the water molecules from the surface, the less they are structured and the lower become their relaxation rate. Changes should be gradual up to reaching the mobility of bulk water, but if this happens in less than 30 μm the used technique is not able to visualize it. Further investigations would require a micro-imaging system.

In spite of this limitation, MR imaging demonstrates the presence of an ordered, low mobility layer of water on the polymeric surface. Pollack and coworkers previously reported that NMR spectra of Nafion powder immersed in water also demonstrate the presence of structured water, as two signals are present, which they attributed to "adsorbed" and interstitial water (which was said to coincide with the EZ) respectively based on chemical shift and relaxation times, stating that no signal was observed for bulk water due to close packing of the powder.[17] We are tempted to say that these two signals should rather be assigned to adsorbed and bulk water respectively, as also suggested by previously published articles.[18] In fact, chemical shift of the higher field peak corresponds to that of bulk water, and while relaxation times measured for the water signal in the Nafion sample are indeed lower than bulk water relaxation time, this difference can reasonably be accounted for by the occurrence of a radiation damping effect, which causes faster magnetization recovery during the inversion recovery sequence.[19,20] The LMZ water signal in NMR spectra would be rather small compared to that of bulk and adsorbed water, and most probably it is hidden under their two peaks. Conversely, MRI allows to clearly distinguish bulk, LMZ and adsorbed water.

Interestingly, the occurrence of a 50 μm layer at the interface between Nafion and water, characterized by higher refractive index, was reported by Bunkin et al. in 2013.[21] The high refractive index zone well correlates with the LMZ observed in the present work. We can reasonably state that the structuring hydrogen bonding might account for both the decreased longitudinal relaxation time and the increased refractive index. On the other hand, in ref.21, the augmented value of the refractive index was justified on the basis of an increased density of water molecules in this area. The authors suggested that water molecules get tightly packed at the Nafion-water interface, because they are embedded into a colloidal array extending beyond the Nafion surface due to extrusion of hydrophilic material in the form of rod-like chains. Of course this could also explain the observed lower mobility of water molecules. Nevertheless, proton density images do not show any difference between bulk and interface water, thus pointing more towards the hypothesis of a layer of pure water with a structured hydrogen bonds array, which not necessarily increases local density but strongly limits molecular mobility.

Although the existence of an LMZ with structured water around the Nafion surface is proven, exclusion does not seem to be related to this property, as the EZ behaves quite differently in respect to the LMZ. At least, the structuring of water molecules cannot be the only mechanism producing the exclusion. In other words, although we cannot exclude that the water structuring which causes the LMZ also contributes to generate the exclusion, other processes, occurring simultaneously in solution, must be taken into account. The EZ is likely the result of a concurrence of phenomena, which may possibly include structuring of water molecules but also movement of particles in ion concentration and/or pH gradients (chemotaxis/diffusiophoresis).[8,9,15,16] Actually, the strong dependence of the EZ on pH, on the

concentration and types of ions in solution and its persistency in cases where the LMZ is not observed at all point more toward the latter hypothesis.

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AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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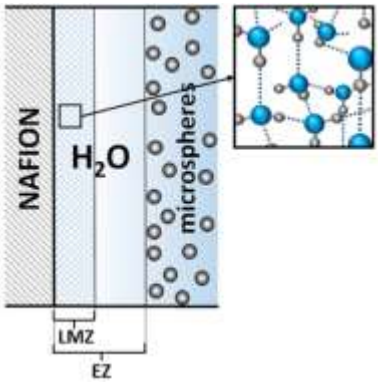
TOC GRAPHICS



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