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Ionic diffusion through a bio-inspired membrane

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1. Introduction

One of the scientific challenges in nanofiltration is to develop nanofilters with both high ion permeability and selectivity, which are often considered as antagonist features. Today, the number of solid state membranes that are readily useable is limited and their performances, i.e. ion permeability and selectivity, are restricted. New materials for nanofiltration are thus clearly requested. On the other hand, it is well known that biological ion-channels insure ionic (Na^+, K^+…) exchange of living cells and that their properties in terms of ionic permeability and selectivity are extremely high. Unfortunately, the transfer of these properties to artificial set-up whose the mechanical strength is high enough to be useful in many different types of applications has not been achieved yet. So, the idea of combining nanoporous solid-state materials with biological ion channel appears as a scientific and technical challenge that could open new perspectives in nanofiltration. Recently [1], we report the first extremely encouraging results on insertion of the ion channel gramicidin A (gA) inside a nanoporous track-etched membrane. These primary results have demonstrated the feasibility for hybrid bio-inspired membrane made of a biological ion channel and a nanoporous polymer material.
The next goal of our project is the enhancement of the hybrid membrane performances in term of ionic selectivity via optimization of the gA confinement inside the nanopores. In this paper, we report the results obtained when the experimental conditions used for the protein insertion are changed : solvent (water/methanol mixture) used for the insertion and temperature. Experimental results on ion diffusion and selectivity through the membrane are interpreted thanks to data obtained from molecular simulation. .

2. Results

We use commercial (nucleopore, Whatman Plc) tracked etched membrane with 15 nm pore diameter (noted Mb15). The as-received membranes are then treated with ethanol prior to gA insertion. Then, gA insertion is realized in different solvent conditions, i.e. methanol/water 5/95 (noted Mb15gAmet) and pure water noted (Mb15gAwat). The characterization of gA in interaction with the nanoporous polymer film is carried out by confocal fluorescence spectroscopy. Typically, the results show the localization of gA inside the nanopores. Ionic diffusion through the hybrid membrane of various chlorine aqueous solutions (KCl, NaCl, $CaCl_2$, $MgCl_2$: 0.1M) are studied (fig.1). For

Mb15gAmet, the apparent ionic diffusion, for all the considered salts, increases when gA is confined inside the nanopores compared to the native membrane. However, this membrane doesn't exhibit ion selectivity. On the contrary, Mb15gAwat exhibits much lower permeability than the native membrane whereas it shows ion selectivity. These results obviously indicate that the solvent used for gA confinement modifies the protein structure and, hence, its functionality.

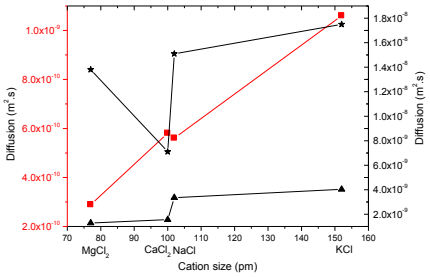

Fig. 1 : evolution of ionic diffusion on Mb15 (black triangles), Mb15gAmet (black stars) and Mb15gAwat(red square) in function cationic ravon radius

These results can be qualitatively explained from molecular simulation based on classical force field molecular dynamics. Indeed, calculation on gA in various methanol/water mixtures shows that the protein has two different possible conformations depending on the methanol molar ratio [2]. It can adopt either a double-stranded β-helix (ds-dimer) or a denatured dimer made of two head-to-head β-helix (hh-dimer) quaternary structures. The ds-dimer is not ion selective while the hh-dimer allows monovalent cations transfer only. Therefore the gA functionality regarding ion diffusion is thought to be much dependent on the solvent composition. It is shown that in methanol/water 5/95, the ds-dimer is the more stable than the hh-dimer. Oppositely, the hh-dimer is more stable in pure water. Calculation of gA confinement inside a modeled carbon nanotube of 7.5 nm diameter confirms these representations. This could explain why no ion selectivity is experimentally measured on membranes prepared with methanol/water solvent and why oppositely ion selectivity is observed when the hybrid membrane is prepared using pure water.

3. Conclusion

This work which is the second stage of a global project aiming at building bio-inspired membranes made of biological ion channels confined inside the nanopores of solid-state materials shows that the solvent used for the protein confinement plays a key role on its conformation, its functionality and therefore on the membrane performances in terms of ion permeability and selectivity.

References

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