

Bottom-up DFT-MD multi-scale modelling of hydrated bulk anion exchange membranes

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Ion Exchange Membranes (IEMs) are key components of various separation technologies in the fields of water treatment, chemicals synthesis and recovery, and energy generation. Generally, IEMs consist in a polymer backbone functionalized with fixed charged groups. When the membrane is put in contact with an electrolytic solution, due to Donnan equilibrium and Donnan exclusion, hydrated ions showing opposite charge with respect to functional charged groups (counter-ions) are selectively adsorbed whereas ions with the same charge (co-ions) are ideally rejected, leading to ion selectivity [1]. The fixed charged groups and counter-ions in the membrane adsorb water leading to a nanophase segregation inside the bulk of the membrane where hydrophobic and hydrophilic domains co-exist (polymer backbone and adsorbed water-solution). Their relative sizes and distribution strongly depend on: membrane materials; Ion Exchange Capacity (IEC, concentration of fixed charged groups); water volume fraction; fixed charged groups and ions' hydration, which have a crucial effect on ion diffusion. Usually, experimental techniques find it difficult to unravel the key structure-kinetic properties relationships, an aspect that can be approached by *ad-hoc* quantum and atomistic models.

In this work, a bottom-up multi-scale methodology to model a series of bulk anion exchange membranes is presented, based on recent published results [2]. First, Molecular Mechanics (MM) of representative polymeric units was used to perform a conformational search of the most stable monomer conformers. Second, *ab initio* calculations in the frame of Density Functional Theory (DFT) of increasingly hydrated functionalized monomers were carried out to define the water uptake per functionalized and non-functionalized monomers, and to parametrize the partial charges later used in the Molecular Dynamics (MD) force field being important parameters controlling morphology and transport features. Third, monomer units were randomly assembled into large polymeric chains to perform MD simulations. Once the simulation boxes were equilibrated through a calibrated simulated annealing protocol, a morphology analysis was performed based on radial distribution functions, cluster analysis of hydrophilic domains as well as 2D density maps to study the percolation degree of the systems. Finally, counter-ion diffusion coefficients were determined at varying IEC and water uptake analyzing the Mean Square Displacement (MSD) curves of counter-ions and by analytical obstruction models based on the water volume fraction inside the membrane. The results refer to polysulfone-tetramethylammonium (PSU-TMA) anion exchange membranes counter-balanced with hydroxide ion [2], and of preliminary results on hydrated PSU-TMA-Cl and polystyrene-TMA-Cl membranes. The results highlight how the *ab initio* methodology for studying the structure-kinetic relationships of the anion exchange membranes is a powerful investigation tool. Moreover, thanks to the minimization of adjustable parameters, commonly adopted in IEMs modelling, it gives general outcomes and can be easily extended to any type of Ion Exchange Membrane material.

[1] T. Luo, S. Abdu, M. Wessling, Selectivity of ion exchange membranes: A review, *J. Memb. Sci.* 555 (2018) 429–454. <https://doi.org/10.1016/j.memsci.2018.03.051>.

[2] J. Luque Di Salvo, G. De Luca, A. Cipollina, G. Micale, Effect of ion exchange capacity and water uptake on hydroxide transport in PSU-TMA membranes: A DFT and molecular dynamics study *J. Memb. Sci.* (2020), <https://doi.org/10.1016/j.memsci.2020.117837>.