



## Tailoring ion exchange membranes to enable low osmotic water transport and energy efficient electro dialysis



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### ABSTRACT

Ion exchange membranes have been applied for water desalination since the 1950s in a process called electro dialysis, ED. Parallel to the transport of ions across ion exchange membranes, water molecules are transported from diluate to concentrate compartments reducing ED efficiency. In this study tailor made meshed membranes were prepared by embedding polymeric meshes with significantly reduced open area into an ion conductive polymer. These membranes were characterized to assess their transport properties. It is shown that by changing mesh open area, material and surface properties, it is possible to significantly reduce osmotic water transport. Polyamide mesh embedded in a cation exchange polymer showed an eightfold decrease of the water mass transport coefficient. Unexpectedly, osmotic water transport was not affected when the same mesh material was embedded in an anion exchange polymer. A decrease of the osmotic water transport for meshed anion exchange membranes was achieved by using a polyethylene terephthalate mesh. Despite the associated electrical resistance increase, application of meshed membranes increased diluate yield and allowed for more energy efficient operation in case ED is confined to a low current density regime.

### 1. Introduction

Electrodialysis, ED, is a well-established membrane desalination technology, primarily applied for the treatment of brackish water [1–7]. Many system designs and material modifications have been introduced in order to apply this process in various industries including the chemical, food, pharmaceutical, semiconductor and wastewater industry [1,8–11]. Moreover, the concept of ion transport across selective barriers can also be used for energy generation in processes like reverse electro dialysis [12–14] and capmix [15–17] and for energy storage applications [18–20]. The key components of these processes are ion exchange membranes, IEMs. A typical IEM consists of a polymeric matrix to which charged groups are fixed [21,22]. There are two types of ion exchange polymers. One with negatively charged groups, such as  $-\text{SO}_3^-$ ,  $-\text{COO}^-$  and  $-\text{PO}_3^{2-}$ , to exclude anions from the matrix, and one with positively charged groups, such as  $-\text{NH}_3^+$ ,  $-\text{NRH}_2^+$  and  $\text{NR}_3^+$ , to exclude cations from the matrix [23]. The first type is called cation exchange membrane (since it blocks anions) and the second type is called anion exchange membrane (since it blocks cations).

Fig. 1A provides an overview of a basic ED process. Cation- and anion-exchange membranes are alternately stacked. The spaces

between the membranes are called compartments and are filled with either porous inert spacers or with ion conductive material to allow solutions to flow along the membranes [24]. On both ends of the membrane assembly two electrodes are submerged in a separate electrolyte ('rinse') solution. In Fig. 1A, salt water enters at the bottom and flows towards the exit at the top. An electric potential is applied at the electrodes. As a result of the electric field, ions will start to move along the field. Due to the charge selectivity of the membranes, part of the ions is blocked. As a result, in half of the compartments, the salt concentration goes down and become fresh ('diluate') and in half of the compartments salt concentration goes up and become concentrated ('concentrate'). In parallel to ion transport across the IEMs caused by the electric field, there is also water being transported from diluate (high water activity close to 1) to concentrate compartments (low water activity), see Fig. 1B. Besides transport of water molecules present in hydration shells of migrated ions, electro-osmosis, water transport can be attributed to osmosis resulting from the chemical potential gradient, and water permeation resulting from a hydrostatic pressure gradient [25,26]. Especially osmosis may contribute to a lower diluate yield and higher energy loss due to decreased electrical current utilization for the actual desalination process [6,19,27,28]. Implications of the osmotic

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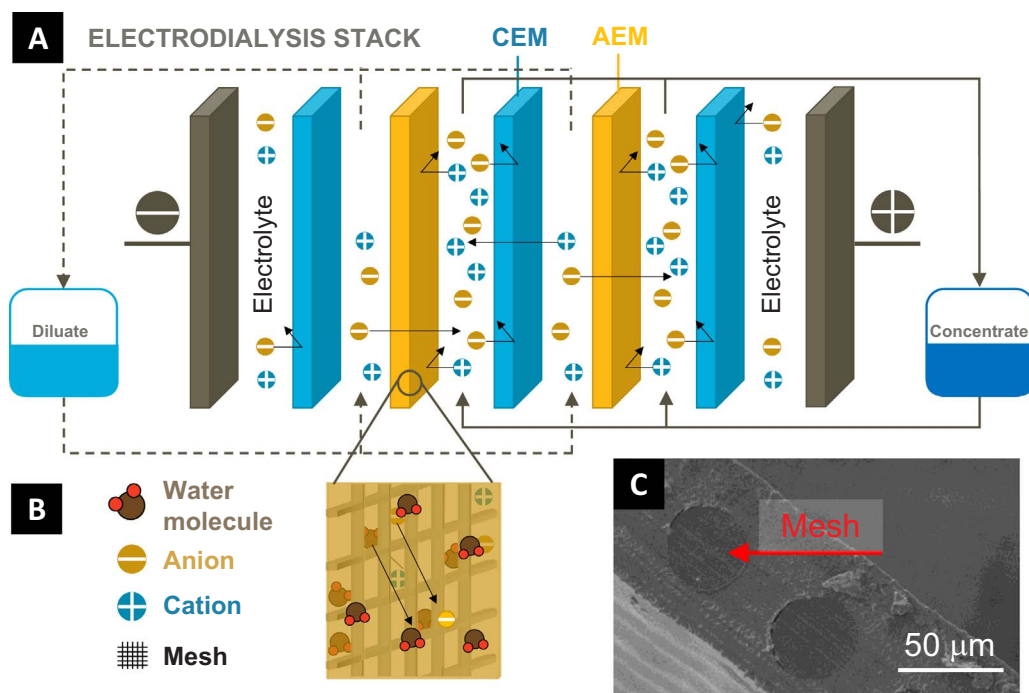


Fig. 1. (A) Schematic overview of the electro-dialysis process. (B) A schematic drawing showing the polymeric mesh embedded with AEM and depicting water transport from diluate to concentrate side. (C) Scanning electron microscope image of an AEM used in this study.

water transport are that ED is ideally operated with a limited concentration difference over the IEMs (i.e. limiting its application), as well as at high current density and hence low energy efficiency. Osmotic transport may be decreased by developing IEMs with low water permeability. Such membranes can be used, for example, for treating the reverse osmosis retentate to produce highly concentrated brines. Another possible application is a separation process where a pure permeate is required.

This study aims to reduce water transport in ED by incorporating a polymeric mesh into an IEM. Fig. 1C shows a scanning electron microscopy picture of an AEM as used in this study. The mesh is completely embedded within the ion exchange polymer, and a continuous dense film of approximately 10  $\mu\text{m}$  thick is covering the polymeric mesh on both sides. We show that it is possible to increase diluate production yield in a batch mode ED process. This is achieved by a reduction of water osmotic transport due to the presence of a low open area mesh within the IEM structure. We also show that the application of meshed membranes increases energy efficiency of ED systems in a low current density regime and at high concentration differences across IEMs (i.e., at a high gradient of water activity). Normally, the low current density at a high concentration differences across IEMs operational range is not available in ED processes due to low energy efficiency in this region and high costs (for more details of energy efficiency analysis see Sections 2.4 and 3.4) [6,19]. Finally, we demonstrated that different polymer mesh materials, surface properties and open areas of the mesh, affect water transport across charged membranes.

## 2. Experimental

### 2.1. Meshed ion exchange membrane synthesis

The ion exchange membranes were prepared using either anionic (FAS solution, 24 wt% of polymer dissolved in N-Methyl-2-Pyrrolidone (NMP); Fumatech, Bietigheim-Bissingen, Germany) or cationic ionomer solution (FKS solution, 16 wt% of polymer dissolved in NMP; Fumatech, Bietigheim-Bissingen, Germany). The membranes without polymeric mesh were prepared by casting 700  $\mu\text{m}$  layer of ionomer solution on top of a glass plate and pre-drying at room temperature under atmospheric conditions to enable slow solvent evaporation. The pre-dried membranes were carefully removed from the glass plate and were dried at 110  $^{\circ}\text{C}$  in a vacuum oven for two days to remove residual NMP solvent. Meshed membranes were prepared as described above, except ionomer solution was casted directly on top of polymeric meshes using a doctor blade. The casting blade was set to 300  $\mu\text{m}$  to arrive at about the same thickness of the dried meshed membranes and the homogeneous membranes. Polymeric meshes made of polyamide (Nitex 03-PA 6.6, Sefar, Switzerland) and polyester (Nitex 07-PET, Sefar, Switzerland) were used as non-conductive meshes. We used three, 60  $\mu\text{m}$  thick, polymeric meshes having different open areas of 18%, 10% and 2%, see Table 1. Surface hydrolysis of polyester mesh was carried out using 2 M aqueous solutions of sodium hydroxide at room temperature for 2 h. After the treatment, the polyester mesh was washed with pure water and dried in a vacuum oven at 25  $^{\circ}\text{C}$  overnight. All prepared membranes have a thickness ranging from 90 to 120  $\mu\text{m}$  in the wet state (see Table 1 for more details).

Table 1

Overview of polymeric mesh parameters. Specific gravity of the Nitex 03-PA 6.6 is 1.14  $\text{g cm}^{-3}$  and Nitex 07-PET is 1.38  $\text{g cm}^{-3}$ .

Membranes	Open area mesh (%)	Mesh thickness ( $\mu\text{m}$ )	Yarn diameter warp ( $\mu\text{m}$ )/ Yarn diameter weft ( $\mu\text{m}$ )	Mesh count, warp ( $\text{n cm}^{-1}$ )/ Mesh count, weft ( $\text{n cm}^{-1}$ )	Mesh opening ( $\mu\text{m}$ ) /Weight ( $\text{g m}^{-2}$ )	Mesh area to volume ratio ( $\text{l cm}^{-1}$ )
Nitex 03-PA 6.6	2%	60	45/31	419/689	7/50	1050
Nitex 03-PA 6.6	10%	60	35/35	513/513	15/40	1140
Nitex 03-PA 6.6	18%	60	40/40	361/361	30/35	1000
Nitex 07-PET	2%	55	47/47	406/457	10/60	850

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