Novel ion exchange Hybrid IEM-NF-Membrane for mMCDI process

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Introduction

The need for fresh water is increasing while the water resources of the world are limited. In Germany the problem of salt contaminated ground water resources by NaCl (sea water intrusion [a]) and NO_3^- (agriculture [b]) are one example needs to be solved.

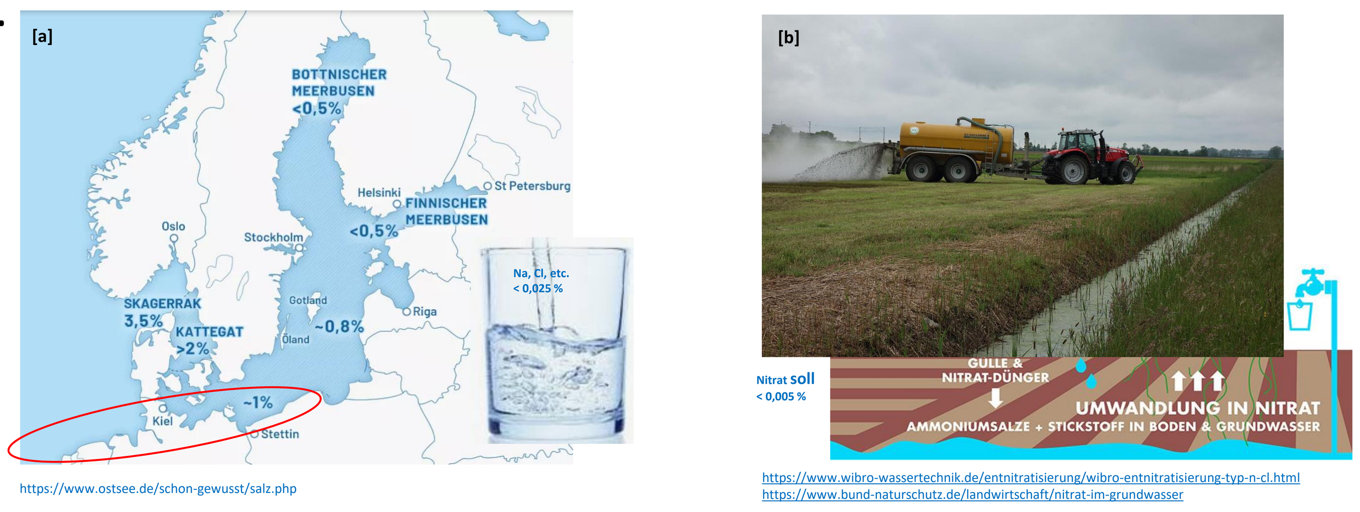


Figure 1: examples of problematic water resources

https://www.ostsee.de/schon-gewusst/salz.php
https://www.wibro-wassertechnik.de/entnitratisierung/wibro-entnitratisierung-typ-n-cl.html
https://www.bund-naturschutz.de/landwirtschaft/nitrat-im-grundwasser

Known processes like Reverse osmosis (RO) or Nanofiltration (NF) are efficient state-of-the-art desalination techniques. However, 100 % desalination is not necessarily required, the opposite for low salt contents in water is true. **M**embrane **C**apacitive **D**e**I**onization (**MCDI**) has recognized as an energy efficient alternative instead of RO and NF. To achieve a selective removal of monovalent ions, monovalent ion selective ion-exchange membranes are needed.

Here we introduce a novel approach for the preparation of monovalent ion selective ion-exchange membranes, referred as hybrid-ion-exchange-NF-membranes.

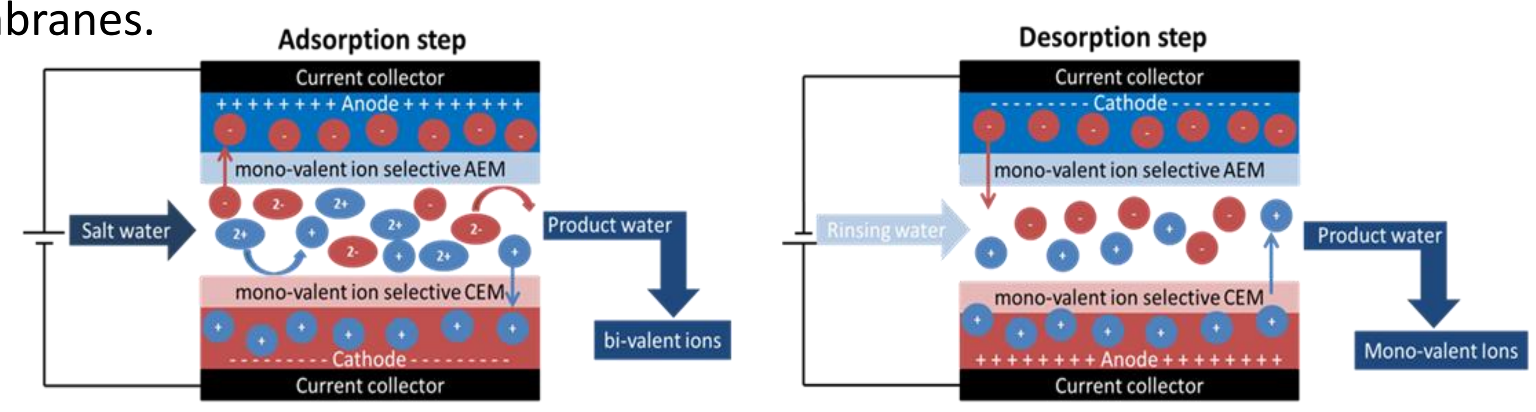


Figure 1: Working principle of monovalent ion selective MCDI (mMCDI)

New Concept for mMCDI

Combining the properties of Nanofiltration membranes (valence selective) and ion-exchange membranes (charge selective)

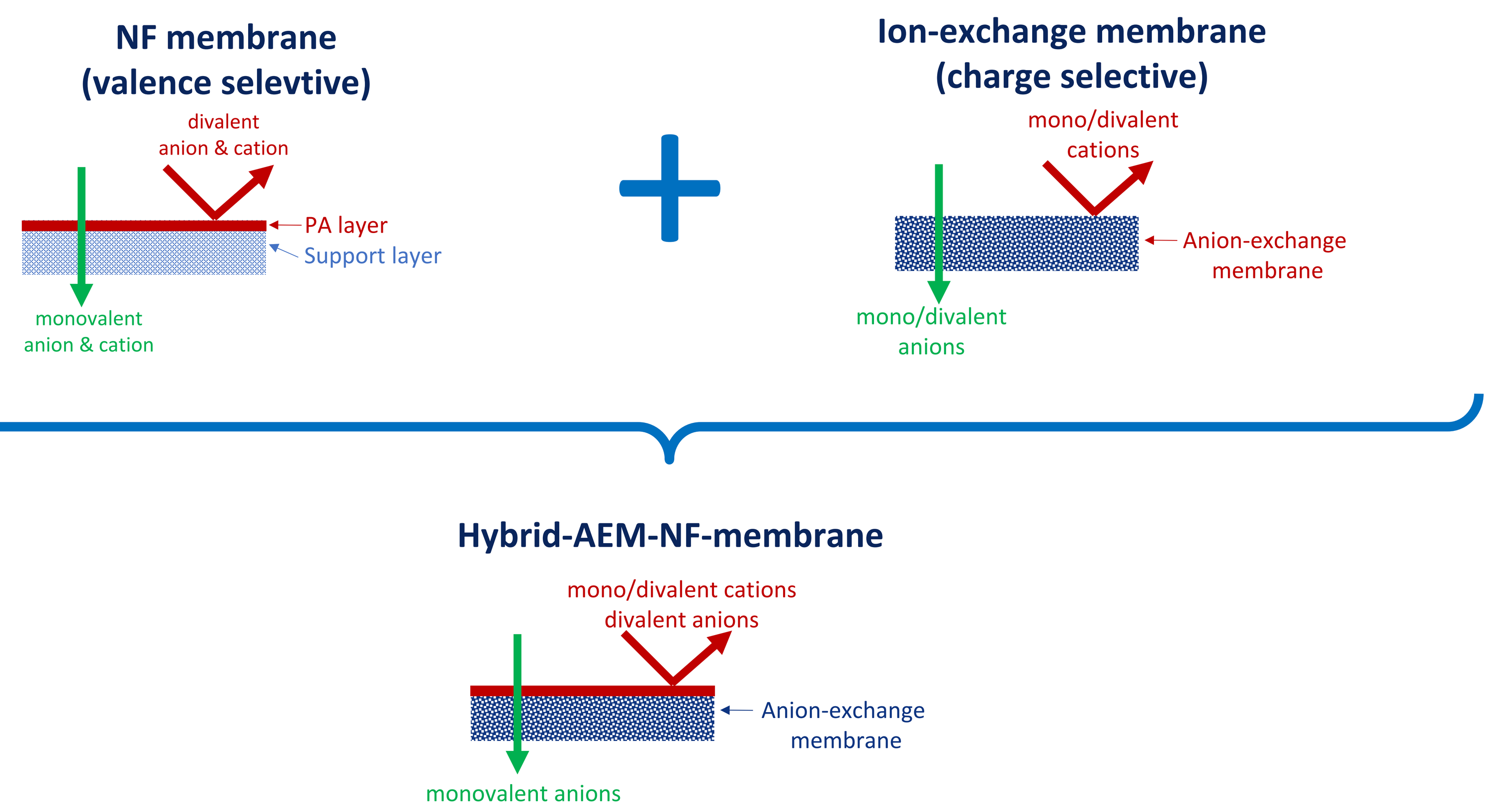


Figure 2: scheme of concept from NF membrane and ion-exchange membrane to hybrid-ion-exchange-NF-membrane.

Experimental

Preparation of ion-exchange membranes

Ion-Exchange membranes are prepared by the pore-filling approach using quaternary di- and tetraallyl ammonium salts for AEM and AMPS with the crosslinker MPA to receive CEM. MicroPES 4F, company 3M Germany, is used as support material. The polymerization is initiated by UV irradiation (365 nm) by the help of DMPA (2,2-Dimethoxy-2-phenyl-acetophenone) with 1 Ma.-% for AEM and AAPH (2,2-Azobis(2-methyl-propionamidine) dihydro-chlorid).

Preparation of hybrid-anion-exchange-NF-membranes

To coat a thin polyamide layer (NF functionality) on the surface of the base membranes a modified interfacial polymerization approach was used. Phenylene diamine (OPD), diaminobenzene sulfonic acid (DABSA) and branched polyethylene imine (PEI) are used as amine components while trimesoyl chloride (TMC) is used as acid component.

Characterization

The membranes are characterized by SEM (morphology), impedance spectroscopy (membrane resistance), membrane potential (permselectivity) and desalination results (valence selectivity in electrodialysis) using binary salt mixtures and DI-water.

Results

SEM

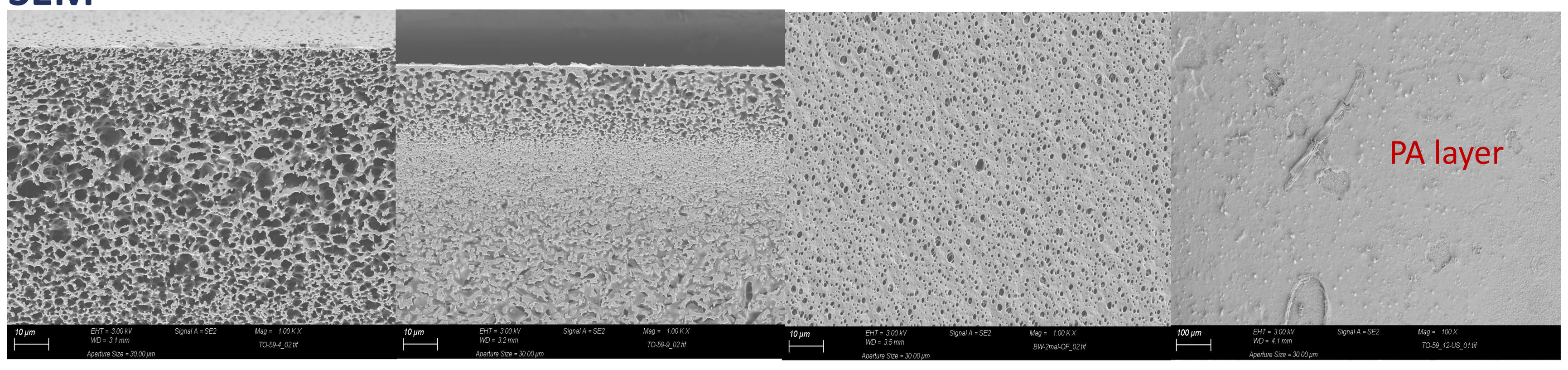


Figure 4: SEM pictures MF-membranes, left unfilled, 2nd left middle filled IE-material, 2nd right middle without polyamide layer on top of membrane, far right with polyamide layer on top of membrane.

- The SEM cross sections (Fig. 4) of the two left pictures show the unfilled and filled membrane prove the successful introduction of the AE-material into the pore volume of the MF membrane. The SEM top view sections (Fig. 4) of the two right pictures give example of the appearance of the polyamide layer covering MF-membranes pores.

Resistance

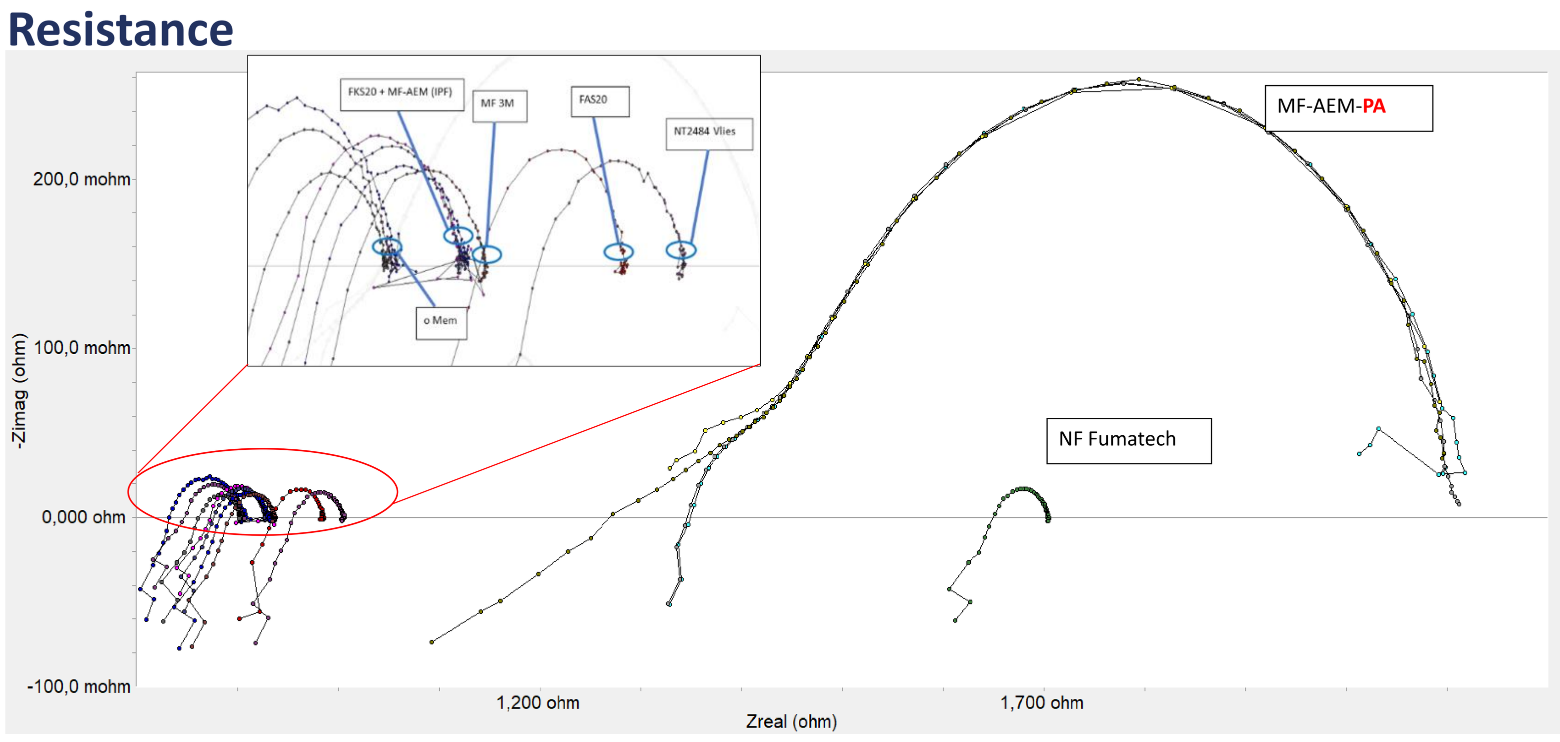
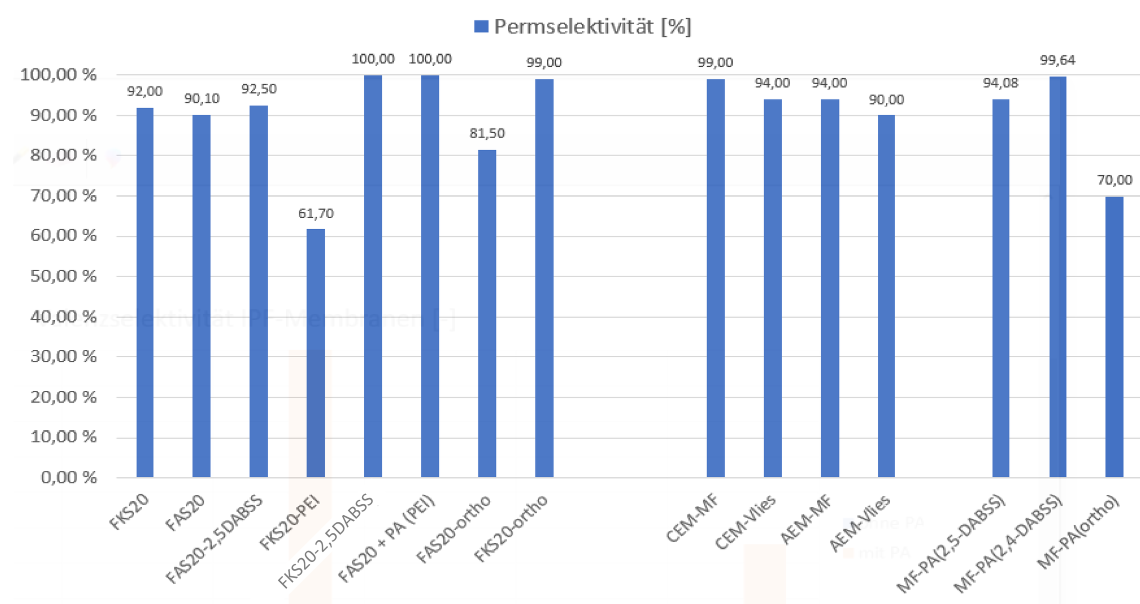


Figure 5: resistances of membranes in nyquist plot.

- The prepared hybrid-AEM-NF-membranes modified with various IE-materials and polyamides show competitive low resistances comparable with commercial membranes (0,93 Ω*cm²) from 0,26 to 0,35 Ω*cm² respectively. In figure 5 a number of membrane examples are shown. The graph on the far-left site is a reference measurement to calculate the membrane resistance from the right intersection of each graph compared with the membrane-graphs. One can see the support-membrane (MF), the filled base membrane (MF-AEM), the commercial membrane (FAS20) and the polyamide coated filled base membrane (MF-AEM-PA) far on the right with a large semi circle.

Permselectivity / Separation Properties



- The application of polyamides lead to distinct differences in valence selectivity (AEM: Cl^-/SO_4^{2-}) of modified membranes and is valuable to adjust specific membrane properties. Measured valence dependent selectivity is much higher after coating with polyamide and especially for opposite charged polyamide. Permselectivity can be found for all membranes in regions from around 90% or even higher.

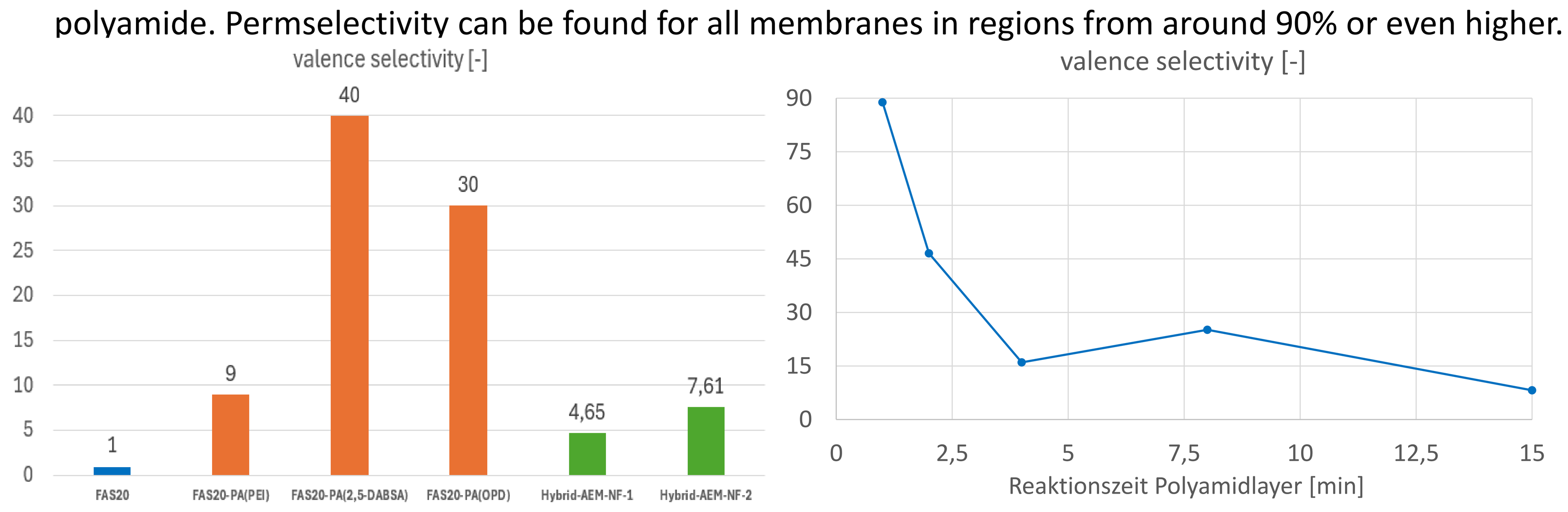


Figure 6: Permselectivity and separation properties of selected membranes

Summary/Conclusion

- Commercial MF membranes proved to be stable and easy-to-use supports for modified membranes.
- A simple, water-based process was developed in which functionalized monomers were crosslinked and polymerized in the pore volume of the MF.
- By coating the AE membranes with an ultra-thin polyamide layer, ions of different valence can be effectively separated in the MCDI process.

Project

innovatION

Partners

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