Journal of Membrane Science 524 (2017) 280–287

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Energy efficiency enhancement of electromembrane desalination systems by local flow redistribution optimized for the asymmetry of cation/anion diffusivity

Bumjoo Kim[a,1], Siwon Choi[b,1], Van Sang Pham[c], Rhokyun Kwak[d], Jongyoon Han[a,e,f,*]

[a] Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
[b] Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
[c] Department of Fluid Mechanics and Ship Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam
[d] Center for BioMicrosystems, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea
[e] Singapore-MIT Alliance for Research and Technology (SMART) Centre, Singapore
[f] Department of Biological Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

ARTICLE INFO

Keywords:
Electrodialysis
Mass transport enhancement
Spacer engineering
Concentration polarization
Ion concentration visualization

ABSTRACT

In an electrochemical system, ion transport near ion exchange membranes or electrodes induces inevitable concentration polarization (*i.e.*, formation of diffusion boundaries), which impedes the mass transport and worsens the energy efficiency. To mitigate the effect of concentration polarization (CP), various efforts towards mass transport enhancement employed structures, often called spacers, which promote mixing and modify the flow velocity distribution in the channel. In this work, we employed an electrodialysis (ED) system as a model to investigate the mass transport effects of embedded microstructures, which can redistribute the local flow velocity. We placed a row of cylindrical posts inside the diluate channel and varied the distance from the posts to the membranes. We studied the effect of this post-to-membrane distance on the mass transport by measuring the current-voltage responses and visualizing ion concentration and flow velocity profiles. The study was done through microfluidic ED model experiments and direct numerical simulation based on the coupled Navier-Stokes and Poisson-Nernst-Planck equations. Our results indicate that when the posts are positioned near the center of the channel, the mass transport is enhanced due to the increase in local convection near the concentration boundary layers. More importantly, we discovered that the mass transport is maximized when the location of the posts is slightly off-centered, due to the asymmetry of the cation/anion diffusivity ($D_{Na+} < D_{Cl-}$). Compared to a system without any structures, the embedded posts can improve both the electrical energy efficiency and the salt removal.

1. Introduction

Currently, reverse osmosis (RO) is considered the leading technology in the field of desalination, and the operation efficiency of RO has been significantly improved over the last two decades, mainly by energy recovery and other optimization. On the other hand, electromembrane desalination can be more advantageous in certain applications due to the flexibility of allowed feed conditions and the low capital cost needed (size of system is generally small). Modeling and optimization of electromembrane desalination systems, such as electrodialysis (ED), have been challenging, largely due to the multiphysics nature of its ion transport process. Despite these challenges, much progress has been achieved in understanding the transport process around ion exchange membranes (IEMs) through experiments and modeling [1–11]. The scientific knowledge obtained from these studies can be solid stepping-stones to be utilized in engineering of electrodialysis and other electromembrane processes, specifically in optimization of spacers in ED.

In an electrochemical system, ion transport near ion exchange membranes and electrodes induces inevitable concentration polarization [12] (*i.e.*, formation of diffusion boundaries) due to the difference in ion transport number between the solution and the IEMs. The resulting diffusion boundary layer (also known as ion depletion region) on the surface of membrane/electrode increases the electrical resis-

* Corresponding author at: Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA.
E-mail address: jyhan@mit.edu (J. Han).
[1] These authors contributed equally in this work.

http://dx.doi.org/10.1016/j.memsci.2016.11.046
Received 30 July 2016; Received in revised form 7 November 2016; Accepted 17 November 2016
Available online 22 November 2016
0376-7388/

tance [13], and hence concentration polarization (CP) is a limiting factor for improving the efficiency of electrodialysis, as well as other electro-membrane processes, including reverse electrodialysis (RED) [14,15] and membrane capacitive deionization [16,17]. Concentration polarization impedes mass transport by creating a high electrical resistance in depletion zones (*e.g.*, diluate channels of ED; see Fig. 1a) and increases the overall energy consumption [14,18]. The effect of concentration polarization will be diminished with an increased intake flowrate [19,20] (Fig. 1b), but only at the cost of a lower salt removal ratio in spite of higher amount of salt removed from the feed solution. Given the fixed intake flowrate, mass transport can be enhanced *via* "mixing promoters", such as spacers [14,18,21,22], corrugated membrane and electrode surfaces [23–27], ion conducting spacer [28,29], pulsating flow [30], and air bubbling [31]. Yet, these methods to reduce the electrical energy consumption are accompanied by a significantly larger pressure drop due to an increased hydrodynamic resistance. Moreover, non-conductive mesh spacers, which are the most common means of mass transport enhancement in the ED and RED practice, have "shadow effect" [28], meaning that parts of membrane/electrode area are "shadowed" by the mixing promoter structures and reduce the effective surface area. The ion conducting spacers do not suffer from the shadow effect, but they are much more costly. An ideal spacer should be able to enhance the mass transport with a minimal increase in hydrodynamic resistance and is made of low cost material. More importantly, the aforementioned methods were developed without considering the asymmetric nature of cation/anion transport although different thicknesses of concentration boundary layers have been observed [32,33].

In this work, we aimed to carry out a systematic analysis of mass transport enhancement in ED processes, by considering the difference in the anion and the cation transport, which arises from their difference in diffusivity. We demonstrated mass transport enhancement in an ED system by employing simple structures (with a relatively small increase in hydrodynamic resistance) inside the diluate channel, which perturb the flow profile locally, as shown in Fig. 1c. These structures re-direct the flow to suppress (or expand) the concentration boundary layers and thus decrease (or increase) the electrical resistance. Our strategy is to maximize the flow velocity near the walls, which results in a relatively reduced flow in the center, to enhance mass transport. While it is in line with the previous studies that reduced resistance with an enhanced flow [19,34], we examined the relation between the overall electrical resistance and the different diffusion boundaries on anion and cation exchange membranes (AEMs and CEMs), *via* experiments and multi-physics numerical modeling. We reveal novel insights on how to engineer optimal spacers given the asymmetric diffusivity of anions and cations in the feed. This is, to the best of our knowledge, the first study to consider the asymmetry of ion pair diffusivity into enhancing mass transport in electromembrane processes.

We demonstrated our ideas in a microfluidic model ED system [32], which can correlate the electrical response of the system with visualization of the flow and the ion concentration profiles. In addition, a direct numerical modeling of the system [35,36] was used in order to elucidate the underlying mechanism behind the observed trends. Combined, the methodologies used in this study provide a well-defined, generally applicable strategy for model-based engineering and optimization of various electromembrane systems such as ED.

2. Methods

2.1. System Setup

The post structures (intended to be representatives of typical "mixing promoters" or spacers, used in previous studies) were only considered inside the diluate channel since the ion depletion boundary and the consequent amplification of electrical resistance is only found in diluate channels. As illustrated in Fig. 1c, D_{post} represents the diameter of posts; d_{CEM} and d_{AEM} are the minimum distance from the post to the CEM and to the AEM, respectively. The distance d′ is defined as the ratio of d_{CEM} to the sum of d_{CEM} and d_{AEM}, *i.e.*, $d'=d_{CEM}/(d_{CEM}+d_{AEM})$. The cylindrical posts were placed in a symmetrical manner around the center (d′=0.5). For example, d′=0.11 and d′=0.89 are equidistant from the CEM and from the AEM, respectively. The average velocities above and below the posts are defined as U_{HP_AEM} and U_{HP_CEM}, respectively. The thickness of the diffusion boundary layers on the AEM and the CEM are termed δ_{bl_AEM} and δ_{bl_CEM}. We only considered the effect of d′ on the boundary layer modification, and hence the size and the frequency of the posts were kept constant.

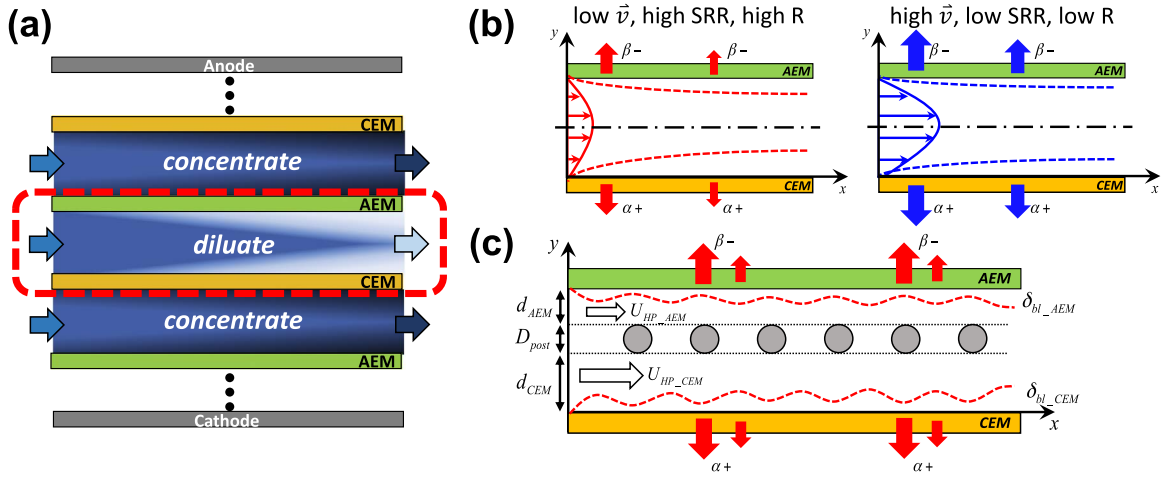

Fig. 1. a) Schematic view of electrodialysis (ED). Color gradient indicates ion concentration profile. Electrical currents and constant forced flow are applied. Post structures are introduced in the red-boxed area whose details are described in b) and c). b) Velocity profile of the solution is drawn with a solid line, and the corresponding diffusion boundary layer for the solution of NaCl (α=Na, β=Cl) is drawn with a dotted line. The arrows represent the flux through the membrane. Blue on the right indicates a higher average velocity, compared to red on the left. A higher velocity results in lower salt removal ratio (SRR) but also a lower electrical resistance (R). c) Description of post geometry. D_{post} represents the diameter of posts; d_{CEM} and d_{AEM} are the minimum distance from the post to the CEM and the AEM, respectively. The average velocities above and below the posts are defined as U_{HP_AEM} and U_{HP_CEM}, respectively. The thickness of the diffusion boundary layers on the AEM and the CEM are termed as δ_{bl_AEM} and δ_{bl_CEM}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)