

A numerical investigation of charged ion transport in electrodialyzers with spacers

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ABSTRACT

Charged ion transport in electrodialyzers with ion mixing spacers was numerically investigated solving Navier-Stokes and Nernst-Planck equations in a three-dimensional Cartesian coordinate system. An electrically non-conductive spacer placed in the membrane channels in the electrodialyzer enhances three-dimensional hydrodynamic and ionic mechanical dispersion, resulting in a substantial increase in the effective mass transfer coefficient over the membrane surfaces. This mechanical dispersion retards depletion of ions and increases the value of the limiting current density, which is of great importance in practical applications of electrodialyzers. Full detailed three-dimensional numerical computations were conducted, for the first time, to investigate the effect of the ion mixing spacers on the limiting current density, using a voxel method based on Cartesian staggered grids along with no-slip velocity and harmonic mean averaging boundary treatments. The results obtained from the three-dimensional numerical simulation were found in good agreement with the experimental data available in the literature.

1. Introduction

Electrodialyzers can be found in various industrial applications, such as brackish water desalination, pharmaceutical and food industrial applications [1–4]. Electrodialysis process possesses its advantages over conventional distillation techniques and the other processes associated with membranes such as those using reverse osmosis [5–7]. In the electrodialysis process, small quantity of dissolved species can be removed away from feed water, whereas, in the reverse osmosis, the large quantity of water must be removed from the feed water. Thus, its required energy consumption is much less than those of the other distillation techniques.

As illustrated in Fig. 1, dilute and concentrate channels are formed using the ion-exchange membranes. These membranes are positioned one after another between the terminal electrodes (i.e. anode and cathode) in the electrodialyzer, such that charged ions transfer selectively through the ion-exchange membranes. Two kinds of membranes, namely, cation and anion exchange membranes, are placed alternately, to form cell units of dilute and concentrate channels. As the charged ions transfer through the membranes under the applied electric field, the dilute cell expels the ions out, whereas the adjacent concentrate cell takes them in. As a result, the bulk ion concentration in the dilute channel decreases whereas that in the concentrate channel increases as

the feed ionic solution flows from the inlet to exit.

Nakayama et al. [8] conducted a boundary layer analysis and showed that it is the thin concentration boundary layer developed over the membrane that determines the electrodialyzer performance. Thus, the boundary layer nature hidden in the Nernst-Planck conservation equation must be fully taken into consideration to investigate the development of the ionic solution boundary layer. In the electrodialyzer, “concentration polarization” is commonly observed, in which the ionic concentration in the dilute channel boundary layer decreases towards the cation exchange membrane (C. E. M.), and the higher ionic concentration in the concentrate channel boundary layer, decreases away from the C. E. M.

In the ionic concentration boundary layer, a steeper concentration gradient at the membrane surface allows a greater electric current (i.e. more charged ions) to pass through the membrane. “Limiting current density” e.g. [4,8,9] is the electric current density which results in zero concentration over the ion exchange membrane as a consequence of excessive polarization of ionic concentration. An electrodialyzer can be operated most efficiently, just under the limiting current density, since, under such an operation, the ionic separation rate attains its maximum, without violating the electro-neutrality. The current density should never exceed the limiting current density. Otherwise, water dissociation takes place within the boundary layer, which increases the electrical

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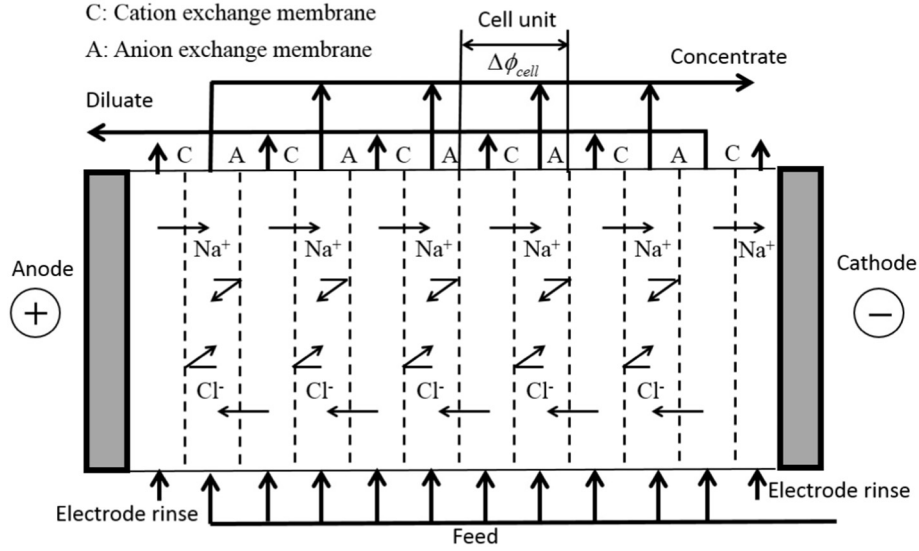


Fig. 1. Electrodialysis stack.

resistance in the dilute solution drastically.

In most industrial applications, the individual ion exchange membranes are separated by an electrically non-conductive net-like spacer, which provides a mechanical support to hold the adjacent cation and anion exchange membranes apart, ensuring a passage for the ionic solutions. Another important function of the spacers is to mix the solutions in the channels. The ionic solutions flowing the channels filled by the net-like spacers follow zig-zag flow paths. This phenomenon commonly observed in a porous medium, namely, “mechanical dispersion”, leads to a substantial increase in the effective mass transfer coefficient over the membrane surfaces, thus, retarding depletion of ions and increasing the value of the limiting current density.

Full detailed three-dimensional computations of such charged ion transport, however, have not been reported yet, since the net-like spacers found in the channel passages in the electrodialyzers are geometrically quite complex, and that the set of three-dimensional governing equations to solve simultaneously is quite formidable. In this study, we shall propose a simplified set of the governing equations based on the assumption of local electro-neutrality, and conduct full detailed three-dimensional numerical computations, for the first time, to investigate the effect of both hydrodynamic and ionic mechanical dispersion brought by the spacers on the limiting current density. We appeal to a voxel method based on Cartesian staggered grids along with no-slip velocity and harmonic mean averaging boundary treatments. The results obtained from the numerical simulation are compared against the experimental data available in the literature.

Some three-dimensional computational investigations of charged ion transport in a spacer-filled compartment and corrugated membrane structure are available in reverse electrodialysis fields [10,11]. However, they are based on the unit cell approach focusing only on the periodically fully developed ionic concentration fields which are not very close to the ion depletion. The present study is unique in the sense that it is the first numerical attempt to reveal the entire three-dimensional ionic concentration field from the entrance through to the exit where the ion depletion is about to take place.

2. Governing equations for charged ionic solution flows

Since the Reynolds number associated with a channel passage is usually small, the ionic solution flow is laminar. The governing equations for incompressible fluid flow, namely, the continuity and Navier-Stokes equations in a tensor form are given as follows:

$$\frac{\partial u_j}{\partial x_j} = 0 \quad (1)$$

$$\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = -\frac{1}{\rho} \frac{\partial p}{\partial x_i} + \nu \frac{\partial^2 u_i}{\partial x_j \partial x_j} \quad (2)$$

where u_i is the velocity vector, p , the pressure, ρ , the density and ν , the kinematic viscosity.

The Nernst-Planck equation in a tensor form describing ion transport of species i in the ionic solution runs as

$$\frac{\partial c_i}{\partial t} + u_j \frac{\partial c_i}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_i \frac{\partial c_i}{\partial x_j} + \frac{z_i F D_i c_i}{RT} \frac{\partial \varphi}{\partial x_j} \right) \quad (3)$$

In the equation, the ionic species is either cation ($i = 1$) or anion ($i = 2$), such as Na^+ or Cl^- . The first term on the right hand side of Eq. (3) corresponds to diffusion whereas the second term corresponds to electrophoresis. Note that D_i is the diffusion coefficient, φ , the voltage, $R (= 8.314 \text{ J/mol K})$, gas constant, T , the absolute temperature and $F (= 96,485 \text{ C/mol})$, Faraday constant. Moreover, z_i denotes the species charge number such that $z_1 = 1$ and $z_2 = -1$ for the case of Na^+ and Cl^- and $z_1 = 1$ and $z_2 = -2$ for the case of Na^+ and SO_4^{2-} .

The Nernst-Planck Eq. (3) is quite formidable, since we have to couple it with (1), (2) and Poisson's equation electrostatics. However, we may follow the procedure presented by Nakayama et al. [8] to simplify the Nernst-Planck equation. In this procedure, we exploit the assumption of local electro-neutrality, namely,

$$z_1 c_1 + z_2 c_2 = 0: \text{Local electro-neutrality} \quad (4)$$

Meanwhile, Eq. (3) can be written for the cation of z_1 and the anion of z_2 , respectively, as

$$\frac{\partial c_1}{\partial t} + u_j \frac{\partial c_1}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_1 \frac{\partial c_1}{\partial x_j} + \frac{z_1 F D_1 c_1}{RT} \frac{\partial \varphi}{\partial x_j} \right) \quad (5a)$$

and

$$\frac{\partial c_2}{\partial t} + u_j \frac{\partial c_2}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_2 \frac{\partial c_2}{\partial x_j} + \frac{z_2 F D_2 c_2}{RT} \frac{\partial \varphi}{\partial x_j} \right) \quad (5b)$$

The summation $D_2 \times (5a) + D_1 \times (5b)$ and the division by $(D_2 - (z_1/z_2)D_1)$ yields.

$$\frac{\partial c_1}{\partial t} + u_j \frac{\partial c_1}{\partial x_j} = \frac{\partial}{\partial x_j} \left(D_e \frac{\partial c_1}{\partial x_j} \right): \text{General ion transport equation} \quad (6)$$

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