SUPPRESSING THE CONCENTRATION POLARIZATION USING POROUS SPACERS IN AN ELECTRO-DIALYSIS DESALINATION

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ABSTRACT
The effect of the structure of spacers on the limiting current density has been investigated in a filter press type electro-dialysis system. We shall introduce 3 types of porous spacers made by 3D printer instead of the conventional mesh spacers. The limiting current density with porous spacers filled in both dilute and concentrate channels has been measured by the stack voltage and pH value for comparing the cases without porous spacers. It has been found that the limiting current density with a porous spacer of the staggered arrangement structure is 1.7 to 3.5 times higher than that without porous spacers. On the other hand, the value of the limiting current density obtained with a porous spacer of the square array structure is lower than that without a porous spacer. It has been found that the concentration polarization within the boundary layer on the membrane can be suppressed by forming a flow toward the membrane due to the mechanical dispersion in porous structures. The active flow mixing by the structure is effective in increasing the current density. Moreover, in this study, the mechanical dispersion coefficient has been estimated from values of the limiting current density by utilizing an analytical solution presented by previous study. In this study, it has been proven that the insertion of porous spacers is quite useful in terms of suppressing the concentration polarization and increasing limiting current density.

INTRODUCTION
Electro-dialysis (ED) has been widely practiced in desalinations for brackish and seawater, deionization of aqueous solutions and salt productions. As shown in Figure 1, salt ions are transported through ion-exchange membranes from one solution to another solution under the influence of an electrical potential difference. The concentration polarization in an electro-dialysis has been investigated in comprehensive experimental studies [1-4]. The concentration polarization takes place within a desalting surface of the membrane, so that salt ions dilute in a boundary layer for the desalting phase. In this time, an electrical resistance increases drastically due to the depletion of the ions within the boundary layer on the membrane. Moreover, when achieving the limiting current density, the water dissociation would take place within a desalting surface of the membrane. This electric current density is termed as “limiting current density”, the acid and alkali generated by water dissociation damage the ion exchange membrane. Thus, it is important to know and increase the value of the limiting current density in an electro-dialysis.

According to Hicks [5], ionic mass transfer increases by inserting mesh spacers in dilute and concentrate channels of an electro-dialysis. Subsequently, a considerable number of experimental investigations [7-12] for the ion transport in an electro-dialysis have been reported for the case of using mesh type spacers. They found that concentration polarization can be suppressed with increasing ionic mass transfer as a result of hydrodynamic mixing of the fluid passing through spacers. Moreover, the value of the limiting current density has increased as improving the structure of spacers [13-14].

In this study, a series of experiments are carried out to increase the limiting current density in an electro-dialysis system by using the present spacers which have porous structures. We shall introduce 3 types of porous spacers made by 3D printer instead of the conventional mesh spacers. According to Nakayama [15], the mixing due to mechanical dispersion in the porous media is much more significant than turbulence mixing. Therefore, the mixing in the present porous spacers can be expected to suppress the concentration polarization and achieve a value of high limiting current density. The effect of porous spacers filled in both dilute and concentrate channels on the limiting current density is elucidated by comparing the cases with and without porous spacers. Moreover, the mechanical dispersion coefficient is estimated from values of the limiting current density by utilizing an analytical solution proposed by previous study [16].

METHOD
We shall introduce 3 types of porous spacers made by 3D printer (Replicator 2X, MakerBot) instead of the conventional mesh spacers. These porous spacers are made by acrylonitrile butadiene styrene. The size of all porous spacers is 700mm × 20mm × 5mm (length × width × height). Figure 2 shows structures of the porous spacers,
which have a number of pores per unit volume as compared with the case of non-porous spacers. Spacer 2 is the square array joined basic structures (shown in Figure 2(d)) which consists of ribs with a diameter 0.64 mm. Spacer 1 and spacer 3 are the staggered arrangement. The structure of the spacer 1 is shifted by the half structure from spacer 2 toward the membrane. On the other hand, the structure of the spacer 3 is shifted by the half structure from spacer 2 toward the vertical direction of the membrane. In this study, a long spacer was made by joining elements (i.e. shown in Figure 2) each other. The specific characteristics for all spacers are tabled in Table 1. In this study, an experimental investigation has been carried out in order to examine the effect of the present porous spacers.

<table>
<thead>
<tr>
<th>Basic structure</th>
<th>a[mm]</th>
<th>b[mm]</th>
<th>c[mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spacer width[mm]</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spacer height[mm]</td>
<td>5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spacer length[mm]</td>
<td>700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porosity[-]</td>
<td>spacer①</td>
<td>0.636</td>
<td>spacer②</td>
</tr>
</tbody>
</table>

In this study, an experimental investigation has been carried out in order to examine the effect of the present porous spacers. The test section is illustrated in Figure 4. In order to make accurate measurements of the stack voltage and the limiting current density, all channel widths W are set to 20mm, such that the effective surface area of an ion-exchange membrane A is L600xW20mm². All distances between membranes H are set to 5mm so as to install the porous spacers. Moreover, the platinum foils of width 5mm are bound between each ion exchange membrane and gasket to measure the stack voltage for 1 unit, namely, which consists of a concentrate phase, a dilute phase, an anion exchange membrane and a cation exchange membrane. In order to establish the fully developed flow to test sections (i.e. ion transport area), an entrance section of 100mm is provided in front of each test section. In this study, 2% NaCl solution was supplied into both inlet dilute and concentrate channels, while, 5% Na₂SO₄ solution was supplied into two electrode channels.

A filter press type electro-dialysis stack used in this experiment is shown in Figure 3, in which cation exchange membranes CIMS and anion-exchange membranes ACS produced by ASTOM co. (Japan) are arranged alternately in the channels for ionic solutions. Platinized titanium plates (DENBOH Co., Japan) are adopted as electrode plates in both anode and cathode. Test sections are constructed by using acrylic plates and rubber gaskets. This electro-dialysis stack consists of two dilute and concentrate channels and two electrode channels, namely, anode and cathode sides.

Figure 4 Test section.
current between the electrode plates in anode and cathode, salt ions are transported from one layer to another layer through ion-exchange membranes under the influence of an electrical potential difference. The diluted and concentrated solutions were sampled at the outlet of dilute and concentrate channels located in the center of the electro-dialysis stack in order to measure solute concentrations and pH values. The concentration and pH value of NaCl and Na₂SO₄ solutions were measured by the multi water quality meter MM-60R (DKK-TOA Co., Japan).

RESULTS

Figure 6 shows the stack voltage for the case of without and with a porous spacer (Spacer 1) under the velocity of each channel \( u=2.0 \) cm/s. As can be seen from Figure 6(a), the stack voltage increases with the current density. Moreover, the stack voltage suddenly rises at a point of the current density, since the electrical resistance in the dilute solution increases due to the depletion of the ions within the boundary layer. This electric current density is termed as “limiting current density (LCD)”. It is found that LCD is 205 A/m² at 2.0 cm/s without a porous spacer. However, as compared with the cases with and without a porous spacer, the stack voltage seem likely to increase in proportion to the current density without reaching the limiting current density by using a porous spacer.

When achieving the limiting current density, the water dissociation would take place within a desalting surface of the membrane. Figure 7 illustrates pH values measured at the outlets of dilute and concentrate channels with and without of a porous spacer for the case of \( u=2.0 \) cm/s and \( C_w=2\% \). It is found that pH value at the dilute and concentrate channels without a porous spacer changes at the same point in which the stack voltage suddenly rises as shown in Figure 6(a), since water dissociation takes place under the limiting current density. On the other hand, in the case with a porous spacer, it is also found a point of dissociating water as shown in Figure 7(b). LCD obtained from pH values is 550 A/m² at \( u=2.0 \) cm/s. This indicates that LCD with a porous spacer is 2.7 times higher than that without a porous spacer at \( u=2.0 \) cm/s.
Figure 8 shows the limiting current density obtained for the case of with and without a porous spacer (Spacer1) under different velocities \( u = 0.5 - 0.25 \) cm/s. As can be seen from this figure, LCD increases with the velocity since the concentration boundary layer thickness decreases with the velocity. Moreover, it is found that LCD with porous spacer is 1.7 to 3.5 times higher than that without a porous spacer. It is proven that the effect of mechanical dispersion on the limiting current density is quite significant. This concentration boundary layer thickness is inversely proportional to ionic mass transfer coefficient. The heat and mass transfer coefficient is known that the value increases in proportion to the 0.5 power. On the other hand, the heat and mass transfer coefficient is found proportional to the velocity due to fluid mixing in porous materials, as indicated by Fu et al. [17] and Nakayama et al. [18]. Thus, further LCD increase can be realized with increasing the velocity.

\[
\text{Figure 8 Effect of porous spacer 1 on LCD.}
\]

In previous study [16], a general ion transport equation for ion solutions was derived from the Nernst-Planck equation by eliminating the electrophoresis term. Moreover, the analytical solutions for predicting LCD were proposed in both cases with and without porous spacer.

- Without a porous spacer

\[
\text{LCD} = 2.366 \frac{FDc_w}{L} \left( \frac{uL}{D_{\text{Na}}W} \right)^{1/3} \tag{1}
\]

- With a porous spacer

\[
\text{LCD} = 1.772Fd_{\text{in}} \left( \frac{uL}{D_{\text{Na}}W} \right)^{1/2} \left( 1 + \frac{D_{\text{dis}}}{D_e} \right) \tag{2}
\]

where \( F \) is Faraday constant (96,485C/mol), \( \varepsilon \) and \( D_{\text{dis}} \) are the porosity of porous spacers and the transverse dispersion coefficient, respectively. The effective diffusion coefficient is given as follows (in this study):

\[
D_e = \frac{2}{\frac{1}{D_{\text{Na}}} + \frac{1}{D_{\text{cr}}}} \tag{3}
\]

A good agreement between the Eq.1 (i.e. in case of without a porous spacer) and the experiment can be seen from Figure 9. Moreover, the transverse dispersion coefficient can be estimated by fitting the data obtained from experiments, as follows:

\[
D_{\text{dis}} = 3.0 \times 10^{-7} uW . \tag{4}
\]

![Figure 9 Determination of the transverse dispersion coefficient.](image)

The effect of the structure of porous spacers on the limiting current density is illustrated in Figure 9. The values of LCD using the spacer 1 or 3 are higher than that without a porous spacer, as a result of mechanical dispersion in porous structures. It indicates that the staggered arrangement has the effect on disturbing the flow in the channel. The effective diffusion coefficient of spacer 3 is estimated to \( D_{\text{dis}} = 1.8 \times 10^{-7} uW \), which is lower than that of the spacer 1. Thus, the depletion of ions within the boundary layer on the membrane can be suppressed by forming a flow toward the membrane. However, the values of LCD using the spacer 2 are lower than that without a porous spacer. The fully developed flow may exist in the square array structure without being disturbed. Moreover, the stagnation of flow on the membrane surface promoted the depletion of the ions within the boundary layer on the membrane. It has been found that active mixing by the structure is effective in increasing the current density.

![Figure 10 Effect of porous spacers on LCD.](image)
CONCLUSIONS
The effect of the structure of spacers on the limiting current density was investigated by using 3 types of porous spacers made by 3D printer. It was found that the value of the limiting current density with a porous spacer of the staggered arrangement is 1.7 to 3.5 times higher than that without a porous spacer. The depletion of ions within the boundary layer on the membrane can be suppressed by supplying a flow toward the membrane. On the other hand, the stagnation of flow on the membrane surface promoted the depletion of the ions within the boundary layer on the membrane, when using a porous spacer of the square array structure. It has been found that active mixing by the structure is effective in increasing the current density. Moreover, it has been proven that the insertion of porous spacers is quite useful in terms of suppressing the concentration polarization and increasing limiting current density.

NOMENCLATURE
A : effective surface area of ion-exchange membranes [m²]
C : concentration of NaCl [%]
D_dis : transverse dispersion coefficient [m²/s]
D_e : effective diffusion coefficient [m²/s]
F : Faraday constant [96,485 C/mol]
H : distances between membranes [m]
I : current density [A/m²]
L : length of test section [m]
LCD : limiting current density [A/m²]
u : velocity [m/s]
W : channel width [m]
ε : porosity [-]

REFERENCES