

## 이온교환막에서의 농도분극 현상

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## Concentration Polarization Phenomena in Ion-Exchange Membranes

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요 약 : 전기투석은 이온성 물질을 분리하고 농축하는데 안정하고 효과적인 공정으로 알려져 있다. 그러나 전기투석 공정은 고가의 이온교환막 때문에 실제 공정에 적용하는데 많은 제한을 받아오고 있다. 따라서 전기투석공정의 운전 전류밀도를 가능한 높게 공급함으로써 이온교환막의 단면적당 flux를 증가시켜 주어야 한다. 그러나 실제 공정의 운전에 있어서 운전 전류밀도는 이온교환막 표면에서의 농도분극 현상으로 제한을 받게 된다. 본 총설에서는 이온교환막을 통한 이온의 이동현상을 설명하고 전류-전압 곡선을 이용한 막특성 분석을 소개하였다. 또한 한계전류밀도 전후의 전류 영역에서 농도분극 현상과 동반하는 전기대류(Electroconvection), 물분해 현상 등에 대한 최근 연구결과를 정리하였다.

**Abstract :** Electrodialysis(ED) is a reliable and effective process for the separation and concentration of ionic compounds. However, commercial uses of ED are often hindered by the cost of the stack that mainly resulted from the ion-exchange membrane cost. In order to minimize the membrane cost, it is desired to operate ED at the highest practicable current density. In an actual ED system, the high current operation is limited by the concentration polarization phenomenon. This article illustrates the transport phenomena of ions through ion exchange membranes using current-voltage relations as a characterizing method. Also recent studies on electroconvection and water-spitting phenomena caused by concentration polarization were reviewed.

**Keywords :** concentration polarization, ion exchange membrane, electrodialysis

### 1. Introduction

Electrodialysis (ED) is an electric potential driven

process in which charged membranes are used to remove ions from an electrolyte solution or to concentrate the solution [1]. The most important application of ED is the production of potable water

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from brackish water [2,3]. Furthermore ED has been widely used in numerous processes from wastewater treatment to applications in the food industries [4,5]. ED process was also suggested as an environmentally friendly alternative to the conventional ionic removal method such as ion-exchange process that gives rise to enormous amounts of salt wastes [6]. With the growing concern over environmental issues, there is a great need for cleaner chemical processes as well as technology to prevent the environmental pollution so that ED process is growing rapidly in the field of separation and chemical processing.

ED is a well-established, reliable and economical method for the separation of ionic compounds. Nevertheless, the widespread commercial use of ED processes are prohibited by the cost of the stack that mainly resulted from the membrane cost. Since the ED process cost is depending on the membrane area, it is desired to operate at the highest practicable current density to get the maximum ion flux per unit membrane area. Operating current levels are, however, restricted by the concentration polarization phenomenon. Based on the classical concentration polarization theory, the current-voltage (I-V) curve of ion-exchange membrane should be linear at low voltage, then increase slowly and finally reach a limiting value [7-9]. No current higher than the limiting current can be expected since the concentration near the membrane has reached zero.

In practice, however, no such limiting value is observed, and the current density continues to increase for high voltage after passing through an inflection point. The current against voltage relation of electric current through ion-exchange membranes at low current densities has been well explained by the Nernst-Planck model [8]. However, the corresponding behavior at high current density is not well understood yet. Thus it is important to understand the mechanism of over-limiting currents because it will enable to develop an advanced ED process which is applicable at a high current density.

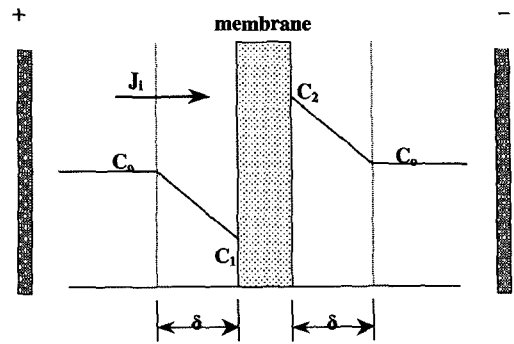


Fig. 1. Schematic diagram illustrating concentration polarization in the diffusion boundary layer of an anion-exchange membrane.  $C_0$  is the concentration of bulk solution,  $C_1$  and  $C_2$  are concentrations on the membrane surface at the depleted and concentrated side, respectively.  $\delta$  is the thickness of diffusion boundary layer.

Recently studies were carried out to operate ED at a current density as high as possible in order to obtain fast desalination with a given membrane area. In this article, the transport phenomena in an ion-exchange membrane at under- and over-limiting current densities were illustrated, focusing on the concentration polarization, convective transport at the over-limiting currents, and water dissociation at the solution/membrane interface.

## 2. Concentration Polarization Phenomena

Although the driving forces, the separation principle and the membranes are completely different in ED from those in pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), concentration polarization may severely affect the separation efficiency. In the ion-exchange membrane system this phenomenon results from the difference in the transport numbers in the solution and that in the ion-exchange membrane [10-13].

Fig. 1. shows a schematic drawing of the net effects of electrical current on the concentration

gradient in the diffusion boundary layer at the membrane surface. In the figure, the so-called Nernst idealization used by defining a boundary layer with thickness  $\delta$ . This assumes a completely mixed zone in the bulk, and completely static zones of solution in boundary layers adjacent to the membrane. When an electric current passes through the membrane system, the current is carried by both types of ions (positive and negative) in the solution phase, whereas it is carried mainly by the counterions in the membrane. The difference in transport number leads to a situation in which the solution close to the membrane surface on the diluate side becomes depleted of salt ions [14,15]. At the same time the concentration near the membrane on the concentrate side increases. Consequently, a concentration gradient is developed in the diffusion boundary layer, and the slope increases with increasing the current density. At a certain current density the concentration of electrolyte on the membrane surface of depleted side reaches zero, leading to a limiting current density (LCD).

According to the classical concentration polarization theory mentioned above, the current should be linear for low applied voltage, increase slowly and finally reach a limiting value. In practice, however, no such limiting value is observed, and the current, after passing through a region of slow variation with potential, continues to increase for high voltages. This implies that the LCD is an ill-defined parameter. Current above the limiting one is referred to as over-limiting current. The typical current-voltage (I-V) curve of highly permselective ion-exchange membrane is depicted schematically in Fig. 2. Three different regions are easily identified in a current-voltage curve. The low current ohmic region (region I) is followed by the plateau (region II), characterized by a much lower slope than that in region I. Inflection of the I-V curve at the plateau is followed by region III, in which the slope of the I-V curve increases again and eventually reaches an asymptotic value which is usually somewhat lower than in

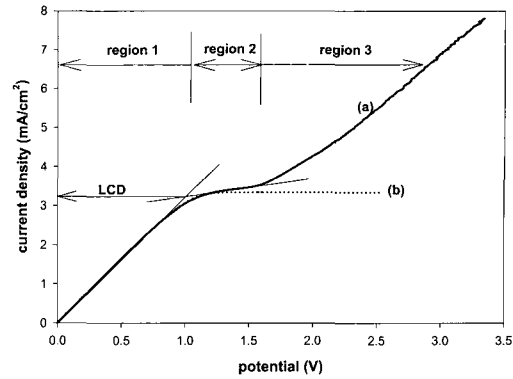


Fig. 2. (a) Typical current-voltage (I-V) curve for an ion-exchange membrane. (b) Current-voltage curve expected from the concentration polarization theory.

region I.

In order to investigate the transport mechanism in an ion-exchange membrane at under- and over-limiting current densities, the characteristic values of the I-V curves were analyzed, such as LCD, plateau length, and the resistance ratio of region III to region I of the I-V curve based on the concentration polarization theory. Current-voltage curves were determined in seven different electrolyte solutions (HCl, LiCl, NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and AlCl<sub>3</sub>). The I-V curves obtained showed the three characteristic regions. We related the LCD values determined experimentally for different electrolyte solutions to the value  $D_+(1-z_+/z_-)$ , which was derived based on the concentration polarization theory, where  $D_+$  is the diffusion coefficient of cation and  $z_+$  and  $z_-$  are the valence of cation and anion, respectively. It was found that the LCD value increased with  $D_+(1-z_+/z_-)$  as expected from the theoretical consideration. The result implies that concentration polarization phenomena can explain the transport of ions through the ion-exchange membrane in the range of under-limiting currents. The differences in the plateau length and the resistance ratio,  $R_{3rd}/R_{1st}$ , with the electrolytes were explained by the Peclet number (Pe). Pe represents the convection pattern and is proportional to the Stokes radius of an ion. Therefore the electrolyte with a greater Stokes

radius may have a more significant convection in the diffusion boundary layer in the over-limiting current region. It was observed that the electrolyte solution with a large Stokes radius had a short plateau length and a lower  $R_{3rd}/R_{1st}$  value compared to the solution with a small Stokes radius [16]. The experimental results suggested that the over-limiting behavior is associated with a kind of convective mixing that develops spontaneously in the depleted diffusion layer at the stage of significant concentration polarization.

### 3. Electroconvection and over-limiting currents

Since the classical concentration polarization theory could not explain the transport mechanism of ions in an ion-exchange membrane at over-limiting current regions, researchers were faced with key problems in explaining why currents above the LCD can be generated and in identifying the physicochemical mechanism responsible. In the early studies on this problem, it was considered that the observed behavior was due to the contribution of ions coming from water dissociation [10,11], electroosmotic flow in the diffusion boundary layer, and loss of permselectivity at a high voltage [17]. However, recent works have shown conclusively that no such mechanisms are responsible for the high current densities observed in ion-exchange membranes [9,18].

Another possible mechanism of over-limiting current was proposed by Rubinstein and collaborators [18-20]. They showed that the existence of over-limiting current could be due to a non-gravitational convection, which Rubinstein calls electroconvection. An ion-exchange membrane is composed of conducting patches and insulating regions, giving a macroscopic heterogeneity (see Fig. 3). In such a situation, the surfaces of equal potential generated in the aqueous electrolyte solution by the applied electrical field are expected not to be oriented parallel to the membrane surface. They are expected to be concentrated at

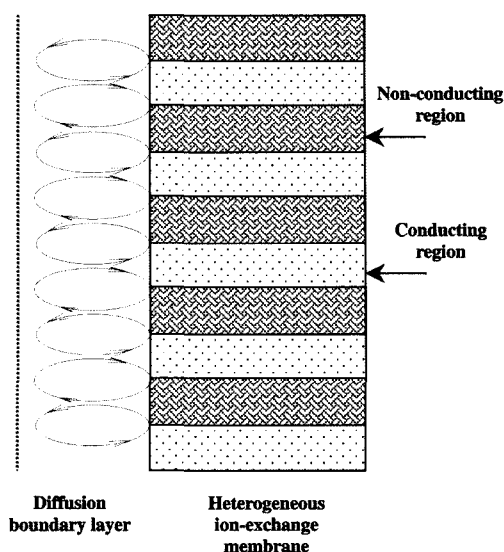


Fig. 3. The schematic view of a two-phase micro-heterogeneous ion-exchange membrane system and the vortices formed in the diffusion boundary layer as a result of electroconvection.

locations at the membrane surface with higher conductivity (conducting patches). The disturbance may be the origin of tangential forces in the diffusion layer. They could generate vortices of convection currents which could lead to a mixing of the depletion layer with the adjacent region of the bulk phase [19]. The increase in the local electrolyte concentration of mobile ions given by the electroconvection would result in an increase in the electrical current passing through the membrane (over-limiting current).

According to the electroconvection theory, the convective mixing at the over-limiting current was resulted from the heterogeneity of ion-exchange membrane. The heterogeneity of different cation-exchange membranes (Neosepta CMX, Selemion CMV, and HJC heterogeneous membrane) was measured quantitatively by chronopotentiometry. Modifying the classical Sand equation, a method has been developed to determine the fractions of conducting regions ( $\epsilon$ ) of the ion-exchange membranes. The values of the CMX, CMV, and HJC membranes were found to be 0.93, 0.95, and 0.75, respectively. Considering the

characteristics of each membrane, i.e. the CMX and CMV are reinforced homogeneous membranes, while the HJC is a heterogeneous membrane, the values determined seemed to be reasonable. In addition it was found that the heterogeneity of ion-exchange membrane was related reasonably to the membrane conductivity, limiting current density and the plateau length of the current-voltage curves of the ion-exchange membranes [21].

To further understand the transport mechanism at the membrane surface, it is highly desirable to measure directly the salt concentration profiles in the vicinity of the membrane. If the over-limiting currents are resulted from the electroconvective mixing in the boundary layer the concentration at the membrane surface would be higher than that of severe concentration polarization. To confirm the convective mixing in the boundary layer the concentration profiles within the layer were directly determined by measuring the potential drops at various current densities, under- and over-limiting regions.

With moving an electrode toward the membrane surface potential drops between the mobile electrode and the other reference electrode (Ag/AgCl) fixed in position were measured. Tapered microelectrode (Ag/AgCl) which had a tip diameter of about 30  $\mu\text{m}$  was used as a mobile electrode. The microelectrode was attached to a 3-D motorized micromanipulator which can control the displacement in the range of 1 to 10  $\mu\text{m}$  [22].

Using the relationship between the potential and concentration, the local salt concentrations at a certain position were obtained by following equation:

$$C(x) = \frac{i(\Delta x)}{\Lambda(\Delta V)}$$

where,  $i$  is current density,  $\Lambda$  the equivalent conductance of electrolyte,  $\Delta x$  the change of distance, and  $\Delta V$  the potential difference between the distance  $\Delta x$ .

From the concentration profiles, that the diffusion

boundary layers were observed in the range of 300-350  $\mu\text{m}$ , which was approximately coincident with the diffusion boundary layer thickness calculated from the limiting current density. Although there were some deviations between the concentrations determined from the Nernst model and from the experiments it was confirmed experimentally that the Nernst model effectively describes the transport phenomena in the ion-exchange membrane system. In addition it was found that the salt concentration at the membrane surface increased when the currents exceeded the limiting current [22]. It was thought that significant concentration polarization formed in the diffusion boundary layer was disturbed by a turbulent convection when the current exceeded the limiting one. As a consequence the concentration at the membrane surface increased to a high level sufficient to generate the over-limiting current.

#### 4. Water-splitting at higher current densities

Frequently the over-limiting current has been related to the occurrence of water-splitting which is considered as an intrinsic property of ion-exchange membrane at over-limiting current. It has been observed that when in the depleted layer the electrolyte concentration falls to extremely low values under the passage of high current,  $\text{H}^+$  and  $\text{OH}^-$  ions take part in the charge transport across the membrane and pH changes appear in the layers adjacent to it. Although it has been conclusively shown that water dissociation at over-limiting current is not significant, i.e. generally less than one percent of the overall current, water dissociation phenomena is critical in operating an ED process because it can lead to pH changes and additional problems, such as scaling on the membrane surface and membrane damage [23].

The mechanism of water dissociation at the over-limiting current density, however, has not been identified clearly. Of various mechanisms proposed,

two noticeable mechanisms are catalytic theory and electric field theory. The former suggests that  $H^+$  and  $OH^-$  ions may be produced in proton transfer reactions between charged groups in the membrane and water molecules [24,25]. The electric field theory explains that water dissociation constant,  $K_d$ , can be increased as much as  $10^7$  times because of a Second Wien effect due to the strong electric field ( $10^8$  V/m) at the membrane-solution interface under the severe concentration polarization [26]. However, many researchers have found that water dissociation is more pronounced with anion-exchange membrane whereas it seems to be of minor importance with cation-exchange membrane [9,27,28]. With regard to the differences of water dissociation between cation and anion-exchange membranes, Simons suggested that the dissociation of water is bound to a thin layer at the surface of an anion-exchange membrane and is caused by a reversible protonation of weakly basic groups such as tertiary amines, which must be present in the membrane [27,28]. This idea has been favored by Rubinstein et al. who found that the water dissociation was reduced when anion-exchange membranes with crown ether groups were used instead of anion-exchange membrane containing quaternary ammonium groups [29].

The water dissociation products can cause the deleterious effects on ED operation so that the water dissociation mechanism should be understood to operate ED process in the over-limiting current region. Water dissociation was examined for both anion- and cation-exchange membranes, and the effects of water dissociation on the structural change of an ion-exchange membrane were investigated. From a series of water dissociation experiments the structural changes of the membranes used were identified by FTIR spectrum employing the internal-reflection spectroscopy technique. It was observed that water dissociation in an anion-exchange membrane (Neosepta AMX, Tokuyama Co.) used at the over-limiting current was greater than that in a virgin

membrane at the same current density. The FTIR study revealed that the tertiary amine groups were formed from the quaternary ammonium groups on the anion-exchange membrane surface where ion depletion occurred under the influence of the applied strong electric field. The occurrence of increased water dissociation was considered to be caused by the protonation and deprotonation reaction of the tertiary amine groups in the anion-exchange membrane. On the other hand there was no structural change for the cation-exchange membrane (Neosepta CMX) under the electric field investigated in this study, which was coincident with the results of water dissociation experiments for the CMX membrane [30].

For economic reasons, it is desired to operate electro dialysis system at a current density as high as possible. To achieve the goal ion-exchange membranes should be chemically stable at the over-limiting current density. It is considered that the conventional anion-exchange membrane containing quaternary ammonium groups is not suitable for an ED system when the processes are operated in the over-limiting current region. To overcome the problem it is recommended to use an alternative functional group, e.g. pyridinium, which is stable under the high electric field condition for the required positive charges of an anion-exchange membrane.

## 5. Concluding Remarks

In many applications, electro dialysis is in direct competition with other separation processes, such as distillation, ion-exchange, and reverse osmosis. It is considered to be more effective than other separation methods in the treatment of waste streams from electroplating, refining, electropolishing and machinery industries [31]. Moreover, this technique was suggested as an environmentally friendly alternative to the conventional ionic removal processes, where more efficient processes are required.

Recent studies showed that operating of electro-

dialysis at over-limiting current region may be possible without significant decrease of current efficiency. However, further studies on chemical stability of anion-exchange membranes have to be achieved for practical applications of this finding. This article may open the way to more stable and efficient utilization of ion-exchange membrane systems in the future.

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