

THE TRANSFER OF CHLORIDE ION ACROSS ANION EXCHANGE MEMBRANE

Zemu Yu, Hanming WANG, and Erkang WANG

*Laboratory of Electroanalytical Chemistry, Changchun Institute of
Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022,
China*

Abstract : The transfer of chloride ion across an anion exchange membrane (AEM) was investigated by cyclic voltammetry (CV) and electrochemical impedance spectra. In CV experiment, when the size of the hole in membrane was much smaller than the distance between membrane holes, the Cl anion transfer showed steady state voltammetric behavior. Each hole in membrane can be regarded as a microelectrode and the membrane was equivalent to a microelectrode array in this condition. When the hole in membrane was large or the distance between membrane holes was small, the CV curve of the Cl anion transfer across membrane showed peak shape, which attributed to linear diffusion. In ac impedance measurement, the impedance spectrum of the membrane system was composed of two semicircles at low dc bias, corresponding to the bulk characteristics of the membrane and the kinetic process of ion transfer, respectively. The bulk membrane resistance increases with increasing dc bias and only one semicircle was observed at higher dc bias. The parameters related to kinetic and membrane properties were discussed.

Keyword : Ion-exchange membrane, Chloride ion, Cyclic voltammetry, ac Impedance spectra.

1. Introduction

Ion-exchange membrane is one of the functionalized membrane investigated and applied earliest. It was extensively applied to the desalination of sea water, the preparation of industrial pure water and the disposal of waste water because of its good selectivity [1,2]. Generally, these applications were carried out by electrodialysis.

In addition, there exist two different descriptions for the permselectivity mechanism of ion-exchange membrane, such as electric double layer and Donnan equilibrium [3]. Therefore, the study of electrochemical process on ion-exchange membrane/electrolyte solution interface is important for its theory and application.

So far, the study on ion-exchange membrane was mainly based on the relations among membrane potential, ion concentration and selectivity as well as new functional membrane [4-6]. The ion transfer process across ion-exchange membranes was rarely studied by electrochemical method, especial voltammetry. Gavach et al. [7,8] investigated the polarization phenomena at the interface between electrolyte solution and ion exchange membrane by analysis of the current density voltage responses and draw the concentration and potential profiles in unstirred layers. Buck et al. [9,10] investigated experimentally and theoretically unusual, non Cottrell behavior of ionic transport in films using voltage steps. Cyclic voltammetry (CV) was rarely applied to study membrane interfacial processes [11-13].

Compared with voltammetry, ac impedance technique is very popular for the study of membrane transfer processes. Buck et al. carried out the theoretical study on ion transfer across membrane under various conditions and set up corresponding model [14-17]. Armstrong [18-21], Cammann [22,23] and other researchers [24 -26] also reported the research results of this area.

Chloride ion exists extensively in sea water and waste water and is one of the most important object for separate ion. In this paper, we have investigated the transfer of chloride ion across an anion exchange membrane by using CV and electrochemical impedance spectra. Our aim is to understand the mechanism of membrane transport and to determine the parameters related to membrane properties.

2. Experiment

Chemicals

Tetraphenylborylsodium (NaTPB) was purchased from Merck Co. and used as supporting electrolyte. Sodium chloride (NaCl, A.R., Beijing Chemical Plant) was used. The water used was of twice-distilled. All experiments were carried out at a laboratory temperature of $(20 \pm 2^\circ\text{C})$.

The membrane studied was polypropylene sebacate anion exchange membrane (PP-ST-DVB, Shanghai Chemical Plant). The thickness of the membrane is 0.18 mm and the area exposed in aqueous solution is 3.14 mm^2 . A four- electrode system was used. Two Ag/AgCl electrodes used as reference one have comparably low resistance and high capacitance in order to avoid interference for the impedance measurement of the membrane. Two platinum plates were used as counter electrode.

Apparatus

In CV experiments, a four electrode cyclic voltammeter with positive IR compensation system was home made [27]. Current-voltage curves were recorded by X-Y recorder (series 60000, Shengyang Precision Instrument Factory).

The equipment used for ac impedance measurements was a Solartron 1250 frequency response analyzer coupled to a TD3690 potentiostat (Tianjing Electronics Instrument Factory) both being controlled by a IBM 386 micro-computer. The

impedance measurements were performed over the frequency range of 65 kHz-0.01Hz. The impedance spectra were analyzed with the help of the "EQUIVALENT CIRCUIT" nonlinear least squares fit program[28].

3. Results and discussion

3.1 CV behavior of chloride anion transfer across anion exchange membrane (AEM)

Because of the high perm selectivity of AEM for anion, we select NaTPB containing large volume anion as supporting electrolyte. The experimental result shows that only very small base current was observed in CV curve when two cells just contain 0.01M NaTPB. However, when we added NaCl solution into one cell or two cells, obvious transfer current appeared due to the transfer of Cl^- across AEM. Fig.1 was the CV curves of system when two aqueous solution contain 0.01M NaTPB and 4.0 mM NaCl They show typical S-shape. The stable

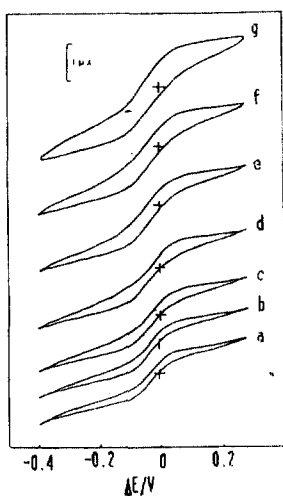


Fig.1 Cyclic voltammograms for the transfer of Cl^- anion across AEM1 at various scan rates two cells with 0.01M NaTPB + 4.0 mM NaCl, Scan rate (mV) a) 10, b) 20, c) 50, d) 100, e) 200, f) 500, g) 1000.

state current does not depend on the linear relationship over the range below 10mM, which further indicates that the stable state currents attribute to potential scan rate (v) at $v < 200\text{mV/s}$ and it increases slightly with scan rate at $v > 200\text{mV/s}$. These results indicate that the diffusion process of Cl^- anion is non-linear. The stable state current increases with increasing concentration of Cl^- anion in solution and shows a good the transfer of Cl^- anion across AEM. When the concentration of Cl^- anion is larger than 12mM, the straight line becomes curved and deviate the linear relation, which may be was caused by the saturation of membrane exchange.

In order to understand further the membrane structure, its scanning electron micrograph was obtained, where exist many small holes distributing unevenly on the membrane and the size of membrane hole is much smaller than the distance between membrane holes.

For this reason, we selected another specification of membrane for CV experiment, the holes of which are large and distribute closely. The experimental results show that the anodic and cathodic branches assume closely S-shape and peak shape respectively at $v < 100\text{mV/s}$. A pair of well-defined peak was observed at $v > 100\text{mV/s}$ (Fig.2).

From the above results, we can explain these experimental phenomena as described in the following. Since the membrane hole is very small ($< \mu\text{m}$ order), each membrane hole can be regarded as a microelectrode while transferring Cl^- anion and the diffusion process assume spherical shape. The membrane is equivalent to microelectrode array however, when membrane holes are large or the distance between membrane holes is small, the diffusion layer formed by the ion transfer overlaps each other, that makes the diffusion on all membrane linear. So the obtained CV curves appear in peak shape as Fig.2.

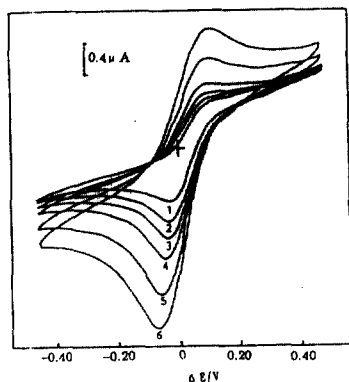


Fig.2 CV curves for the transfer of Cl^- anion across AEM1 at various scan rates
two cells with 0.01M NaTPB + 4.0 mM NaCl,
Scan rate (mV) a) 10, b) 20, c)50, d) 100, e) 200,
f) 500, g) 1000.

3.2 Electrochemical impedance of the transfer of Cl^- anion across AEM

Usually, the electric equivalent circuit corresponding to a membrane in a symmetrical PTFE cell (two current-carrying electrodes and two Ag/AgCl reference electrodes) can be shown in Fig.3(a) [29]. It consists of the bathing solution resistance R_s , the bulk membrane resistance R_b , the charge-transfer resistance R_{ct} and

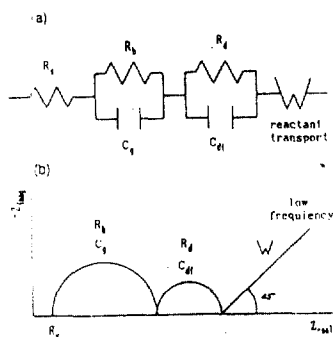


Fig.3 a) An equivalent circuit to PTFE system
b) Impedance plane plot corresponding to the components in a).

the Warburg impedance. C_g and C_{dl} represent the geometric capacitance and the double layer capacitance respectively.

As in Fig.3, the first semicircle corresponds to the bulk membrane resistance, R_b ; the second semicircle in the low frequency range corresponds to the charge-transfer resistance, R_{ct} , and is the charge-transfer process across the membrane-solution interface, and the straight line corresponds to the Warburg impedance.

Impedance plots were analyzed using the commercially available program(EQUIVCRT.PAS) for the non-linear least-squares fit (NLLSF). From the analysis results, it was found that the bulk membrane resistance (R_b) was $3.71 \text{ k}\Omega/\text{cm}^2$ charge-transfer resistance R_{ct} was $0.68 \text{ k}\Omega/\text{cm}^2$. ion-exchange current, j_0 across the membrane could be calculated from the equation [26] $j_0 = RT/nFR_{ct} = 37.1 \mu\text{A}/\text{cm}^2$.

4. Conclusions

The transfer of chloride ion across AEM was investigated by using CV and electrochemical impedance spectra. CV experimental results indicate that the Cl^- anion transfer showed steady state voltammetric behavior when the size of the hole in membrane was much smaller than the distance between membrane holes. Each hole in membrane can be regarded as a microelectrode and the membrane was equivalent to a microelectrode array in this condition. When the hole in membrane was large or the distance between membrane holes was small, the CV curve of the Cl^- anion transfer across membrane showed peak shape, which attributed to linear diffusion. In ac impedance measurement, the impedance spectrum of the membrane system was composed of two semicircles at low dc bias, corresponding to the bulk characteristics of the membrane and the kinetic process of ion transfer,

respectively. The bulk membrane resistance increases with increasing dc bias and only one semicircle was observed at higher dc bias. The related parameters were obtained as the bulk membrane resistance as $3.71 \text{ k}\Omega \text{ cm}^2$ and the charge-transfer resistance (R_{ct}) was $0.68 \text{ k}\Omega \text{ cm}^2$ and the ion-exchange current (j_0) across the membrane was $37.1 \mu\text{A cm}^{-2}$.

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6. References

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