



Study of electric mass transfer peculiarities in electromembrane systems by the rotating membrane disk method



Mikhail Sharafan*, Viktor Zabolotsky

Department of Physical Chemistry, Kuban State University, Stavropolskaya Str., 149, 350040, Krasnodar, Russia

HIGHLIGHTS

- A rotating membrane disk (RMD) with horizontally positioned membrane is described.
- The method for simultaneous recording of CVC and transport numbers of ions is developed.
- The coupled phenomena of concentration polarization were analyzed.
- Electrochemical characteristics of monopolar and bipolar asymmetric membranes were studied.

ARTICLE INFO

Article history:

Received 30 June 2013

Received in revised form 20 November 2013

Accepted 16 December 2013

Available online 3 February 2014

Keywords:

Ion-exchange membrane

Current-voltage characteristic

Water dissociation

Diffusion layer

Limiting current

Electric mass transfer

ABSTRACT

This study examines one of the current issues of membrane electrochemistry: the study of ion transport patterns through membranes under high and ultra-high current densities. It focuses on the new mechanisms for their delivery to membrane/solution interface, the role of concentration polarization coupled phenomena and its impact on intensification of mass transfer in electromembrane systems (EMS). Furthermore, an experimental device consisting of a rotating membrane disk (RMD) with horizontally positioned ion-exchange membrane is described. The device's design makes it possible to simultaneously obtain current-voltage characteristics (CVCs) and dependences of effective transport numbers for ions of electrolyte and water dissociation products on the current density. Partial CVCs are calculated and limiting current densities and diffusion layer thickness are determined at various disk rotation rates. It was established that the coupled phenomena of the concentration polarization are the reason for the distortion of the classic CVC form with a horizontal plateau. Such behavior observes even under conditions when the diffusion-layer thickness is stabilized by the RMD method. It was described that in the studied asymmetric bipolar membranes (aBPM) the ratio of chemical reaction part (water splitting at bipolar border) and electrodiffusive part of overall mass transfer shifts towards chemical reaction at high rotation speed.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

The widespread use of ion-exchange membranes in wastewater treatment processes and the production of drinking water, water for microelectronics and other areas provide an in-depth study of the properties of ion-exchange membranes and ion transport patterns at high and ultra-high current densities. Relevance of work to intensify the mass transfer in electro-membrane systems (EMS) is obvious, since is the path to the creation of high-performance membrane apparatus, much-needed modern membrane electrochemistry. It is not a coincidence that the study of the phenomena is related to the concentration polarization at the interface membrane/solution since it is top priority in the application of electrochemistry.

Development of a general theory for EMS overlimiting state is restrained by the delay of the experimental investigation of the mass transfer mechanisms under overlimiting currents from theoretical base. The main reason for the delay are hydrodynamic conditions near the membrane surface, namely the difficulty of maintaining and controlling the diffusion layer thickness near the surface of the membrane, as well as the role of the adjacent membranes or electrodes in the studied electromembrane system. Diffusion layer thickness depends not only on the geometry and size of electrochemical cells or an electro dialysis membrane channels, but also on the longitudinal coordinates of the membrane. Reduction of the diffusion layer thickness causes a decrease in concentration polarization, an increase in the limiting current value and the current efficiency of the process. In practice, the integral characteristics of the EMS with averaged value of the diffusion layer thickness are measured. This makes it difficult and, in some cases, impossible to check the experimental theory. Progress in this direction has been made due to the fundamental works aimed

* Corresponding author.

E-mail address: Shafon80@mail.ru (M. Sharafan).

at the study of the ions transport processes through membranes under intense current regimes, including usage of rotating membrane disk (RMD) method. The RMD method was created based on the classic hydrodynamic theory by V.G. Levich, developed in the 50s for a system with a rotating disk electrode (RDE) [1]. The diffusion layer thickness may be made constant over the entire surface of an ion-exchange membrane and controlled by varying the electrode's rotation rate. All this makes the RMD a unique tool for studying EMS [2–7]. However, these studies had a number of deficiencies one of which is that they could not measure transport numbers of ions simultaneously with total CVC. At high current densities, when numerous effects of concentration polarization complicate classical ion electrodiffusion transport phenomenon, it is insufficient only to register polarization characteristics of membranes. It is necessary to simultaneously measure ion fluxes (effective transport numbers of ions) with the registration CVC of EMS. This method and system with RMD were first developed and patented by the authors [8]. As a result, ion-exchange membrane CVC and Hittorf transport numbers can be obtained simultaneously at a constant thickness of the diffusion layer. The fact strongly extends functionality of the RMD method. The RMD method, proposed in [8], makes it possible to evaluate quantitatively the contribution of the conjugated effects of concentration polarization in the overall mass transfer for a various ion-exchange membranes under overlimiting currents regimes. It is important to stress the practical significance of the work, as the knowledge of structure and properties of the membrane opens up the way for the creation of membranes with improved physical and chemical characteristics and technical-economic parameters for a new generation of high-intensity electro dialysis (production of ultrapure water) based on these membranes. At the same time, improvement of the deep desalination efficiency and demineralization with simultaneous pH correction (for the needs heat and power engineering or for carbon dioxide removal from the solution) requires an accurate selection of membrane pairs with clearly defined role of the concentration polarization conjugate effects. Due to the RMD, the experimental evaluation of the role of the concentration polarization conjugate effects is possible now.

This work is aimed at using the RMD method to investigate the electric mass transport regularities of a binary electrolyte and water dissociation reaction at the membrane/solution interface in various EMS.

2. Experimental

Materials for this investigation include the heterogeneous cation-exchange membrane MC-40 (Russia) and asymmetric bipolar membranes (aBPM)¹ in contact with 0.001 M sodium chloride solutions. The procedure used for the creation of these aBPM membranes is described in [9,10]. Ralex AMH-Pes was used as an anion-exchange layer (thickness of 450 μm) and Nafion™ type membrane as a cation-exchange layer (thickness of 10 μm) on the investigation aBPM. The main advantage of such membranes (aBPM) is the ability to adjust the ratio of the functions of transport of salt ions and generating products of water dissociation by modifying the thickness of one layer constituting the bipolar membrane. CVCs in this EMS were measured under galvanostatic conditions with a step-wise increase of current density in the apparatus with an RMD. Technique to study membrane systems using a RMD method is described in detail and tested in [8,11]. The RMD rotation rate was varied within the limits 100–500 rpm. In this interval laminar liquid flow was observed near the membrane [1,8]. The experiments were carried out at a temperature of 25 ± 0.5 °C. Further in the research [11] the voltamperometry method and Hittorf's method of transport number measurement were used. These methods were combined in the invented RMD installation (Fig. 1) to record

electro-mass transfer of salt ions and water dissociation products in EMS MC-40/0.001 M solution NaCl and aBPM/0.01 M solution NaCl.

3. Results and discussion

The experimental procedure was as follows. Simultaneously with the recording of a total CVC (Fig. 2) for the membrane/solution system in the solution collected from the upper half-cell of RMD (2 Fig. 1), we determined values of pH and electroconductivity, from which we calculated its composition. The solution composition was additionally monitored by a direct chemical analysis. Data on the solution composition variation were used when calculating Hittorf's transport numbers and a partial, by current, CVC (Fig. 3).

For finding the values of the limiting electrodiffusion current in the systems under investigation, total (Fig. 2) and partial (Fig. 3) CVCs were smoothed as before [11] by means of the approximating equations:

$$i = a_1 \frac{e^{a_2 \Delta \phi} - 1}{e^{a_2 \Delta \phi} + 1} + a_3 (e^{a_4 \Delta \phi} - 1), \quad (1)$$

$$i_H = a_3 (e^{a_4 \Delta \phi} - 1), \quad (2)$$

where a_1 – a_4 are numerical coefficients, and $\Delta \phi$ is the potential drop (in V).

Analysis of the CVCs for the EMS with MC-40/0.001 M NaCl has shown that the limiting current increases with an increasing RMD rotation rate. However, the classic CVC form with a horizontal plateau at the limiting current is distorted (Fig. 2). It is known that the major reasons for the current density boost at $i > i_{lim}$ are: the dissociation of water at the membrane/solution interphase boundary and the induced exaltation effect of the limiting current [12–16]; the emergence of a space-charge region near the membrane/solution interface [17]; the emergence of electroosmotic convection in the near-membrane region due to the interaction between the solution with violated electroneutrality and the external electric field [18,19]. As a result of these phenomena, the diffusion layer thickness δ diminishes and the current density at $i > i_{lim}$ rises. Hence the distortion in the classic shape of CVC that is typical for the electrode and membrane systems with the electrodiffusion mechanism of the ion transport.

To estimate the contributions to the total mass transport from the water-dissociation products and the exaltation effect, the partial CVC for sodium ions and hydrogen ions (Fig. 3) were calculated. The well-known Kharkats equation [15, Eq. (13)] was used to calculate the contribution from the exaltation effect. It is clear from Fig. 3 that the water dissociation reaction proceeds rapidly in the system. Calculations show that for a potential difference of 4.5 V in this system water dissociation contributes 30–35% of the total mass transport, while the exaltation effect contributes 7–8%.

In addition to the heterogeneous membrane MC-40 characteristics of EMS with asymmetric bipolar membranes (aBPM/0.01 M NaCl) were investigated: total and partial CVC were measured, and limiting current densities and diffusion layer thickness were determined at various disk rotation rates.

Comparison of the experimental data was carried out by the characteristic linear dependence $i_{lim} - \sqrt{\omega}$ (Fig. 4). The limiting current for the all EMS was calculated in accordance with the theory of Levich by means of the equations:

$$i_{lim} = \frac{FD^*c_0}{(1-t_1)\delta_0}, \quad (3)$$

$$\delta_0 = 1,61(D^*)^{1/3} \nu^{1/6} \omega^{-1/2}, \quad (4)$$

¹ The authors are thankful S.S. Melnikov for the samples asymmetric bipolar membranes.

Download English Version:

<https://daneshyari.com/en/article/623562>

Download Persian Version:

<https://daneshyari.com/article/623562>

[Daneshyari.com](https://daneshyari.com)