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Water splitting at an anion-exchange membrane as studied by impedance spectroscopy

Ekaterina Kniaginicheva [a], Natalia Pismenskaya [a], Stanislav Melnikov [a,*],
Ekaterina Belashova [a,b], Philippe Sistat [b], Marc Cretin [b], Victor Nikonenko [a]

[a] Kuban State University, Physical Chemistry, Membrane Research Institute, Stavropolskaya Street, 149, Krasnodar 350040, Russia
[b] European Membrane Institute, CNRS-ENSCM-UMII, CC047, Place E. Bataillon, 34095 Montpellier Cdx 5, France

ABSTRACT

Electrochemical impedance spectroscopy (EIS) is largely used in studying water splitting reaction in bipolar membranes (BPMs). This reaction is also very important in monopolar membrane systems, where it constitutes one of the possible mechanisms of the overlimiting current conductance. However, despite of 60-year research history in this domain, there are only a few studies where EIS was applied. Apparently, it is due to poor understanding of AC response of monopolar membranes in overlimiting current range where charge transfer by electrodiffusion competes with current-induced convection and water splitting products transfer.

For the first time, we propose a mathematical description of monopolar membrane's impedance spectra associated with water splitting. We show that these spectra are of the Gerischer type, as in the case of BPMs. The boundary value problem takes into account the proton-transfer catalytic mechanism of water splitting. The solution of this problem is in a good accordance with experimental spectra found for an AMX-SB membrane at differenat biased DC currents. It is found that the effective rate constant of water splitting reaction increases with increasing DC current, similar, as in the case of BPMs.

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1. Introduction

One of the ways to enhance mass transfer in electrodialysis (ED) with ion-exchange membranes is the use of overlimiting current mode [1,2]. In this mode, electrodiffusion of ions is coupled with such effects at the membrane/solution interface as generation of H+ and OH− ions [3–6] and electroconvection [7–10]. To study these phenomena, voltammetry and chronopotentiometry are usually used [2, 7,11–13], sometimes combined with the measurement of solution pH on the inlet and outlet of the ED channel [13]. Electrochemical impedance spectroscopy is rarely applied to study the behaviour of monopolar membranes under a biased direct current (DC) [14–17]. However, this method is proven effective in study of electrode processes [18,19], ion and water transport in fuel cells [20], as well as in bipolar membranes (BPMs) [21–23]. A BPM is the simplest membrane system for studying water splitting. Effectively, in BPMs, this reaction occurring at the bipolar junction is the main electrochemical process. The concentration profiles of H+ and OH- ions are symmetric in

each monopolar layer [24] (Fig. 1a), and a simple equivalent circuit consisted of series-connected ohmic resistance and Gerischer impedance describes well the impedance spectrum [23,25]. The monopolar membranes involved are nearly ideally selective [26].

The impedance of an electrochemical system with a monopolar membrane is more difficult to describe, mainly due to asymmetry of the concentration profiles at the interface. As in the case of BPMs, the rate of water splitting depends on the catalytic activity of the fixed groups with respect to the water dissociation reaction. It depends also on the electric field intensity and the rate of H^+ and OH^- ions removal from the reaction zone. One can imagine that the reaction zone occupies some boundary region of the membrane. Apparently, it does not involve the external solution phase, since in this phase the water dissociation reaction proceeds very slowly [27]. The main part of the reaction zone should be within the EDL on the membrane side where an electric field of high intensity accelerates the reaction [27].

Generally, the simulation of monopolar membrane EIS is a complicated problem, its analytical and numerical solutions are found so far only for the currents lower than the limiting one [16,28–30].

The aims of this work is modelling and experimental study of the overlimiting ion transfer across an anion-exchange membrane accompanied by the water dissociation reaction at the membrane/

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* Correspondence to: Kuban State University, Stavropolskaya Street, 149, Krasnodar 350040, Russia.

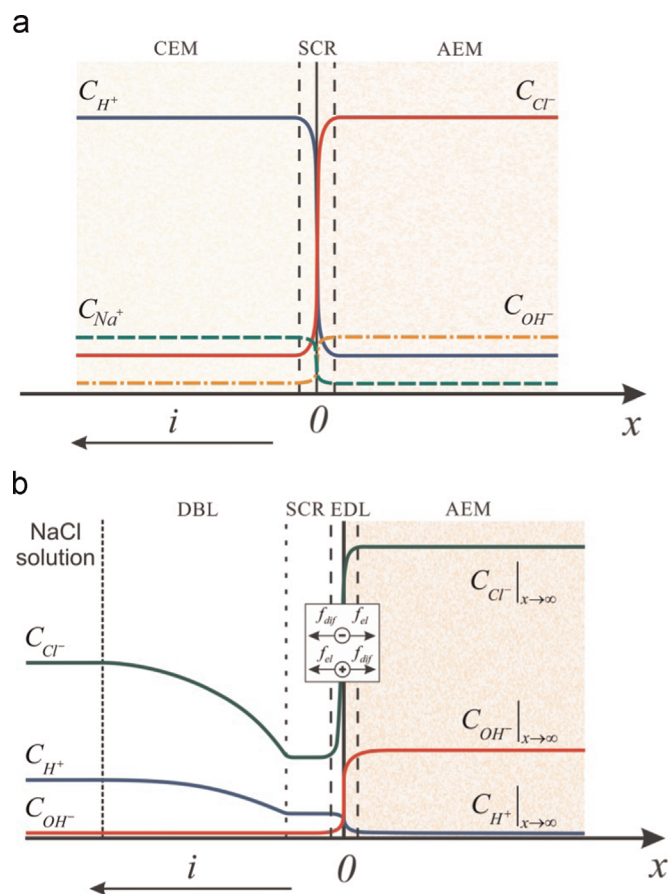*E-mail address:* melnikov.stanislav@gmail.com (S. Melnikov).

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Fig. 1. Concentration profiles near the interface of a bipolar (a) and a monopolar anion-exchange (b) membranes at overlimiting current density where water splitting reaction occurs. Abbreviations: CEM and AEM: cation-exchange and anion-exchange membranes, respectively; EDL: equilibrium electric double layer; SCR: extended space charge region (where the concentration of counterions, Cl−, is dominant); DBL: diffusion boundary layer. The thicknesses of the layers are not to scale.

solution interface. The EIS is used together with the measurement of the pH difference between the outlet and inlet solutions. Special attention will be paid to the changes in the impedance spectrum caused by the water dissociation reaction.

2. Experimental

A homogeneous anion-exchange Neosepta AMX-SB (Astom, Japan) membrane was studied. Though the catalytic activity of fixed quaternary ammonium groups of this membrane [31] in respect to water splitting is low, it is known that this membrane splits water with a moderate rate at overlimiting currents [32].

To study the electrochemical impedance spectra of the membrane, a four-chamber electrochemical cell, described in [31], was used. The compartments adjoining the membrane under study were separated from the electrode compartments by a MK-40 CEM. The distance between the neighbouring membranes (h) was 6.5 mm. The membrane active surface area was 2×2 cm^2. The average linear flow velocity (V) of a 0.02 M NaCl solution in each chamber was 0.4 cm/s. Two Luggin capillaries connected with Ag/AgCl electrodes were used for potential difference measurement. The capillaries were placed from each sides of the membrane under study at approximately 0.8 mm from its surface in the centre of the chamber.

The impedance spectra were measured by using an Autolab-

100 (EcoChemi, The Netherlands) electrochemical complex supplied with the FRA2 attachment and Nova 1.8 software.

Prior to measurements, the cell was kept for 20 min under the same DC current density as used as the biased current in impedance measurements. The impedance spectra were measured in the 3 mHz-130 kHz frequency range starting from the lowest frequency. The AC signal amplitude was 0.06 mA cm^{-2}. In parallel to impedance measurements, continuous control of pH at the inlet and outlet of the desalination channel was performed with HANNA HI 98107 pH-metre.

The theoretical limiting current density for the anion-exchange membrane ($i_{\lim}^{theor}$) was calculated by the convection-diffusion model using the Lévêque equation [7], which gives for the experimental conditions of this work $i_{\lim}^{theor} = 3.1$ mA cm^{-2}.

After obtaining an impedance spectrum, the studied membrane was removed from the cell and the impedance measurement was repeated without the membrane. The impedance of the membrane was found by subtracting the real and imaginary impedance components of the cell obtained with and without the membrane [16].

All experiments were performed at a constant temperature of 25 ± 0.5 °C.

3. Results

As Fig. 2 shows, for currents lower than the limiting one ($0 < i/i_{\lim}^{theor} < 1$), a monopolar membrane's impedance spectrum can be divided into two arcs [33,34]. The first one occurring in the 130–10 kHz frequency range is due to the circuit composed of a geometric (bulk) capacitance in parallel with an ohmic resistance related to both (polarised) diffusion layers and the membrane bulk. The second arc (occurring at $f < 10$ Hz) is due to the EDL capacitance, in parallel with the finite-length Warburg impedance [16], for the left and the right interfaces.

With increasing biased DC current density, the electrolyte concentration in the depleted diffusion layer decreases, its ohmic resistance increases, which leads to the increase in the diameter of the first semicircle (Fig. 2a).

When the DC current reaches $i_{\lim}^{theor}$, a new component appears on the impedance spectrum of the membrane in a medium frequency range (10 Hz–10 kHz). This component can be attributed to the Gerischer impedance caused by a homogeneous chemical reaction. In membrane systems under intensive polarisation, it is the water splitting at the membrane/solution interface [27]. With increasing current, the water splitting rate increases and the Gerischer impedance arc grows.

When $i/i_{\lim}^{theor} > 1.5$, water splitting becomes the dominant process and all three regions of the impedance spectrum merge into one arc. When $i/i_{\lim}^{theor} > 2$, the total resistance of the membrane system starts to decrease, probably due to the emergence of a large amount of highly mobile H$^+$ and OH-ions in the depleted diffusion layer and partial transition of the membrane into OH$^-$ form.

The above transformations of the spectra are consistent with the changes in the pH difference between the outlet and inlet solutions, ΔpH. For the analysis below, let us note that in NaCl solutions, the limiting current density at the AEM ($i_{\lim A}^{theor}$), is nearly 1.5 times higher than that at the CEM ($i_{\lim C}^{theor}$) [12] due to higher mobility of Cl$^-$ ions in comparison with that of Na$^+$. In a desalting compartment formed by an AEM and a CEM, the limiting current density is the lowest of $i_{\lim A}^{theor}$ and $i_{\lim C}^{theor}$ that is $i_{\lim C}^{theor}$: when the current density approaches $i_{\lim C}^{theor}$, the resistance of the compartment grows rapidly.

When $i < < i_{\lim}^{theor}$, the water splitting reaction does not occur, and ΔpH$=0$. At currents near the limiting one, ΔpH> 0, hence pH