



Heterogeneity of heterogeneous ion-exchange membranes investigated by chronopotentiometry and X-ray computed microtomography



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ABSTRACT

Chronopotentiometry is a powerful experimental technique for characterization of ion-exchange membranes, especially phenomena associated with ion transport and the occurrence of overlimiting current. One also uses this technique to estimate heterogeneity of ion-exchange membranes, or more precisely the fractions of conductive and nonconductive regions in the membrane, by measuring so called transition times and their substitution into Sand equation. Here, we test this approach on small pieces of heterogeneous cation- and anion-exchange membranes by combining two experimental techniques, namely chronopotentiometry and X-ray computed microtomography. While chronopotentiometry provides data for the theoretical analysis based on Sand equation, microtomography provides a detailed analysis of the membrane structure both on its surface and in its volume. Such a structural analysis allows for evaluation of volumetric and surface fractions of ion-exchange resin and also quantification of the surface area of the active ion-exchange material on the depletion side of the membrane. We compare the experimental data from both techniques to see how they correlate and discuss the obtained results. We conduct the same experimental investigation on single ion-exchange resin particles which are a component of the aforementioned heterogeneous membranes. The ion-exchange particles can be viewed as homogeneous ion-exchange systems. Our structural analysis by means of the newly developed technique based on micro-computed tomography showed that the volume and the surface compositions of the heterogeneous membranes differ. The surface fraction of the ion-exchange resin is two to three times smaller than the corresponding volumetric fraction. The experimental transition times showed very good agreement with the predictions of the Sand equation in case of the ion-exchange particles. Unlike that the transition times were not well predicted by the Sand equation in case of the heterogeneous ion-exchange membranes. This fact along with observed differences in the structure of these membranes on their surface and in their volume limit the use of the Sand equation to estimate the content of the ion-exchange resin in these membranes.

1. Introduction

Electrodeionization [1] and electrodialysis [2] are important industrial electromembrane separation processes which are widely used e. g. for water purification, water desalination, desalination of food products and many others [3]. The units for electrodialysis and electrodeionization contain a stack of often heterogeneous ion-exchange membranes in which so called cation and anion-exchange membranes alternate [4]. Heterogeneous ion-exchange membranes, in most encountered embodiments, consist of three major components: (i) functional ion-exchange material in the form of finely ground ion-exchange resin particles with relatively wide particle size distribution, (ii)

polymeric binder encapsulating the ground resin and (iii) polymeric fibers providing mechanical strength. The structural heterogeneity of the membranes given by the use of different materials also reflects in the electrochemical properties of the membrane [5]. While the ion-exchange resin is electrically well conductive, the binder and polymeric fibers are nonconductive which in standard heterogeneous membranes leads to creation of well conductive domains randomly distributed within nonconductive binder. Our recent study on a structure of a cation-exchange membrane has shown that (i) these membranes also contain relatively large amount of macropores which interconnect the resin particles and (ii) these membranes change their structure significantly upon swelling [6].

Abbreviations: PE, polyethylene; PES, polyester; μ -CT, X-ray computed microtomography; IEM, ion-exchange membrane; CEM, cation-exchange membrane; AEM, anion-exchange membrane

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It is widely known that the ion-exchange membranes display a nonlinear current-voltage curve characteristic for ion-selective systems. One can clearly distinguish three typical regions on such a curve that are referred to as (i) underlimiting, (ii) limiting, and (iii) overlimiting [7–9]. While the first two regions have been well understood and explained, the last one is still investigated intensively. The main reason is that there are several different mechanisms contributing to the occurrence of the overlimiting current and the dominant mechanism is largely given by the type of the membrane, experimental arrangement and the composition of the electrolyte solution adjacent to the membrane. Still, two major mechanisms causing the overlimiting region are recognized in the scientific community and these are: (i) electroconvection [10,11] and (ii) water splitting [12,13]. Several papers have been published clearly showing an effect of the membrane structure on electroconvection [10,14]. Recently, the scientific community has started to concentrate on setting such conditions so that one could operate electrodialysis units in the overlimiting region. The use of higher electric currents would enable intensification of the ED processes [15] which in turn could bring economical savings with respect to the area of the membranes needed [13]. This, however, requires thorough understanding of processes setting in under given conditions which is another reason why the structure of the used membranes is so important.

The structure of a heterogeneous ion-exchange membrane also determines intrinsically its properties such as resistance, selectivity towards transport of ions, etc., which affect the performance of the ion-exchange membranes and its efficiency in removal of given ions. Recent studies on heterogeneous ion-exchange membranes have also revealed a significant effect of structural and thus implicitly conductive heterogeneity on the shape of current-voltage characteristics [14] and electrokinetic behavior of the membranes [16–18]. For example, Balster et al. [14] showed that: (i) commercial homogenous cation exchange membranes possessing some degree of microheterogeneity had a shorter plateau lengths than those membranes covered with a cationic layer, which was explained by the increase in the structural heterogeneity of the membrane, (ii) commercial heterogeneous cation-exchange membrane displayed shorter plateau than any homogenous ones, and (iii) artificially corrugated membranes with the thickness of undulation in the range of boundary layer thickness had shorter plateau than the flat membranes. Volodina et al. [16] reported that the local limiting current density through conductive regions of heterogeneous ion-exchange membranes is several times higher than the average limiting current density of a studied homogenous ion-exchange membrane. This observation was explained by lateral diffusion of the electrolyte from neighboring non-conducting regions and by coupled convection. However, the limiting current density related to the overall membrane surface is usually lower in the case of heterogeneous ion-exchange membranes when compared with homogenous ones [19]. It was also shown that patterning of the membrane (introduction of heterogeneities) can cause early onset of electroconvection and thus eliminate diffusion-limited transport which is responsible for the limiting current and the occurrence of the limiting region on the CVC [20]. For this reason, the limiting current density related to the overall membrane surface area may in some situations be even higher for heterogeneous ion-exchange membranes than for homogeneous ones [10]. Higher tendency of heterogeneous ion-exchange membranes towards water splitting and the occurrence of electroconvection is also attributed to their intrinsic heterogeneity given by random alteration of conductive and nonconductive domains [16]. The conductive regions create spots of local electric field enhancement. It is a general understanding that such heterogeneity on the membrane surface contributes to the onset of vortices [17].

One of the most referenced models which describes heterogeneity of ion-exchange membranes is called microheterogeneous model [13,21]. This model depicts the membrane as a two-phase system where one phase is the ion-exchange gel and the other is the electroneutral

solution. The properties of the membrane are then expressed as functions of the properties of both phases and their volume fractions. This model has been applied to homogenous membranes where it was used to link the membrane structure to its electrochemical properties such as conductivity, permeability and permselectivity. In case of heterogeneous membranes, one also has to add another phase to the aforementioned model corresponding to the nonconductive polymer which functions as a binder [18].

Chronopotentiometry is an experimental technique in which constant current load is applied on a membrane system usually with stagnant layers of adjacent electrolyte solutions and the voltage drop is measured as a function of time. This technique is often used to characterize ion-exchange membranes [22] and to study fundamental behavior of these membranes [18,23] both in underlimiting [24] and overlimiting regions [25,26]. The constant DC current load (if sufficiently large) causes formation of depletion and concentration regions in the electrolyte solutions on either side of the membrane, a phenomenon known as concentration polarization [8,27]. The eventual result of the concentration polarization is the decrease in the electrolyte concentration on the depletion side of the membrane almost to zero. The event of reaching a thin layer of electrolyte solutions with almost zero concentration of the electrolyte is reflected on a chronopotentiometric curve as a sudden increase in the potential drop. The time required for the system to reach this sudden increase in the voltage drop from the beginning of the application of the current load is called the transition time. One can predict transition times theoretically by using a so called Sand equation. The theory resulting in the Sand equation is based on solving unsteady one-directional diffusional problem in an electrolyte solution on the depletion side of the membrane. Since this theory is well known, we only state the final form of this equation here and refer the reader to other articles nicely explaining its derivation [20,29]. The final form of the Sand equation written for simple, uni-univalent electrolyte solution such as KCl (used in this work) is usually given as:

$$\tau_s = \frac{\pi D_s}{4} \left(\frac{c_0 z_j F}{t_j^M - t_j^S} \right)^2 \frac{1}{i^2} \quad (1)$$

In this equation, τ_s is the transition time predicted by the Sand equation, D_s is the diffusion coefficient of the electrolyte, z_j is the charge number of the counterion, F is the Faraday constant, t_j^M is the transport number of the counterion in the membrane, t_j^S is the transport number in the solution, and i is the current density. The diffusion coefficient of the electrolyte is calculated from:

$$D_s = \frac{2D^+D^-}{D^+ + D^-} \quad (2)$$

in which D^+ and D^- are diffusion coefficients of the cation and the anion in water solutions, respectively. To apply the Sand equation on the experimental data, one has to (i) know the transport number of the counterion in the membrane, and (ii) to calculate the experimental current densities from the knowledge of the applied current and the surface area of the ion-exchange membrane. While the transport numbers for a given membrane are usually given by the manufacturer of the membrane and the current is known from the experiment, the surface area is not determined that easily. One usually uses the area of the membrane that is defined by the outer sealing of the membrane in the experimental system. Such an area, however, includes both conductive (active) and nonconductive domains, which leads to calculation of current densities lower than those that effectively develop in the real system (the current focuses into conductive domains). In these cases, the Sand equation usually predicts longer transition times. However, one can adjust (decrease) the area of the membrane to a value which would increase the current densities so that the resulting transient times computed from the Sand equation would agree with the experimentally obtained ones. This strategy was used by Choi et al. [18] who

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