Swelling induced structural changes of a heterogeneous cation-exchange membrane analyzed by micro-computed tomography

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ABSTRACT

3D reconstruction of heterogeneous ion-exchange membranes when swollen in an appropriate electrolyte by micro-computed tomography (μ-CT) can provide important information on structural changes caused by their swelling or shrinkage and used this knowledge along with their electrochemical characteristics for optimization of the structure of these industrially important polymeric composites. We developed a methodology that allows scanning of swollen membrane samples while not being immersed in the solution, a condition necessary for μ-CT analysis of polymeric samples. Qualitative description of membrane swelling and shrinkage induced by volume-changing ion-exchange resin particles demonstrates their strong effect on structural changes in the membrane and identifies salt concentration as one of the major factors affecting the extent to which the membrane swells or shrinks. Experimental study focused on investigating the effect of salt concentration reveals that membrane volume decreases with increasing salt concentration. The dependence between the volume of the membrane and the concentration was well fitted with a natural logarithm. This fit can be used as an empirical equation for estimating the volumetric changes of the membrane caused by immersion in salt solutions of different concentrations.

1. Introduction

Heterogeneous ion-exchange membranes (IEMs) are functional composites widely used in industrial electroseparation processes mainly for water purification (e. g. electrodialysis, electrodeionization, etc…) [1]. These membranes consist of three major components: (i) finely ground ion-exchange resin particles (resin powder), (ii) polymeric binder, and (iii) reinforcing polymeric fibers [2,3]. Ion-exchange resin for ion-exchange membranes is usually copolymer of styrene and divinylbenzene which is functionalized with chemical groups providing the required property to exchange either cations or anions. In case of strong ion-exchangers, quaternary ammonium groups bearing positive charge when solvated are used in anion-exchange resin and sulfone groups bearing negative charge when solvated in cation-exchange resin [4]. Ion selectivity [5] of these particles towards ions contained in the surrounding solutions is given by electrostatic repulsion and attraction forces. The polymeric binder is usually polyvinylchloride, polyethylene or polypropylene and its main role is to bind the finely ground resin particles together. The polymeric fibers are mostly made of polyester or polyamide and they improve mechanical stability of the membranes. These membranes are produced as large sheets by lamination when ground ion-exchange resin particles are blended with binder pellets, slightly melted and laminated between two cylindrical rollers along with reinforcing fiber mesh that is placed on both sides of the membrane [1]. The structure of these membranes is thus characterized by (i) random distribution of ground ion-exchange resin particles within the binder, and (ii) wide size distribution of the functional ion-exchange resin. The structure of heterogeneous ion-exchange membranes, which cannot be very well controlled during manufacturing, however, affects both mechanical and electrochemical properties of these functional composites [6] which in turn influence the performance and reliability of large electroseparation industrial units. There is a significant effort devoted to production of optimized heterogeneous ion-exchange membranes [7]. For instance, 3D profiling of ion-exchange membrane by heat pressing against a mold has been used to produce defined structures on the membrane surface. These molded membranes exhibited improved transport characteristics when compared to the original untreated membranes. Enhanced transport across molded membranes was attributed mainly to the increase in active area of these membranes, i. e. the area on the membrane surface occupied by ion-exchange resin particles [8].

The structure of these membranes does not only influence their

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electrochemical characteristics, it also strongly affects the electrokinetic behavior exhibited by these membranes [9,10]. When connected in DC electrical field that is typically applied in electrodialysis, the unequal flux of counter- and co-ions through the membrane caused by the ion selectivity displayed by the membranes results in generation of depletion and concentration regions in the electrolyte adjacent to the membrane [11,12]. When one applies DC voltage that is larger than the critical, electrohydrodynamic vortex appears on the depletion side of the membrane. One of the theories elucidating the occurrence of the vortex builds on the heterogeneous structure of the membrane [13] creating spatial heterogeneity in electrical conductivity of the membrane [14]. Randomly distributed ground ion-exchange particles exhibiting high ionic conductivity are surrounded by nonconductive binder or fibers. The electrical field, which focuses into the conductive regions, distorts from the original direction and drives the electrohydrodynamic vortex [10].

The actual structure of these membranes is commonly studied in a dried state by means of analytical techniques allowing only surface analysis [15]. These studies suffer from two major drawbacks: (i) they do not characterize the volume of the membranes that largely contributes to the overall electrochemical properties, and (ii) they cannot capture the structural changes associated with swelling of the membrane when immersed in a water solution. Interesting data describing the structure of the membranes can be obtained by contact porosimetry. Contact porosimetry evaluates among others distribution of volume of pores as a function their nominal radii ranging from 1 nm to 100 μm [16]. These studies revealed that characteristic radius of pores in ion-exchange material is about 10 nm [17]. However, this technique does not allow spatial reconstruction of the heterogeneous materials.

It is generally known that IEMs have significantly different volumes between a dry and wet state [18]. Ion-exchange resin particles are highly charged macro-porous or gel systems and their exposure to water or electrolytes results in their swelling [19]. The theoretical description of swelling of polyelectrolyte gels (as e. g. ion-exchange resin) is still incomplete and a subject of theoretical and experimental research [20,21]. The major contributing factors are thermodynamic mixing (chemical potentials of the solvent, i. e. water, outside and inside the particle have to be the same), osmotic pressures as a result of different concentrations of solutes inside and outside the particle and electrostatic interactions given by the presence of the fixed charge [22,23].

To be able to (i) analyze the whole volume of the heterogeneous ion-exchange membranes, (ii) evaluate structural changes in the membrane caused by swelling and (iii) describe the structure of the fully swollen membrane, i. e. the membrane that can be used in electrodialysis, we embarked on developing a technique allowing to exploit computed tomography [24,25] for the reconstruction of the membrane 3D structure. Computed tomography exposes the sample under study with X-ray and collects the information about X-ray attenuation in the sample by using a detector. By collecting a set of images capturing the attenuation of X-ray when the sample is exposed from various sides, one can distinguish domains exhibiting different absorption properties towards X-ray, and thus different materials of which the sample consists. One problem that arises in scanning polymeric samples immersed in water is in high absorption of exposing X-ray by water causing undesirable loss in contrast among the scanned polymers. We developed a technique that overcomes this problem by scanning the swollen polymeric samples in saturated water vapor preventing the sample from drying. Using this technique, we performed an experimental study looking at structural changes brought about by swelling the heterogeneous ion-exchange membrane in KCl solutions of various concentrations.

2. Material and methods

2.1. Materials

The studied heterogeneous cation-exchange membrane (CEM) was kindly provided by a Czech company MemBrain a.s. This particular membrane contains polyethylene (PE) as a binder and polyester (PES) as reinforcing fibers. The other materials and chemicals used in this work included: DI water desalted by reverse osmosis (conductivity 3 μS/cm), KCl purchased from Penta a.s. Czech republic, UV curable acrylic glue Acrifix 192 (produced by Evonik), silicone for mold making N1522 purchased from Elchemco a.s. Czech republic.

2.2. Methods

2.2.1. Sample preparation

We cut out a small piece (cca 1×1 mm^2) of the heterogeneous CEM and embed the membrane in the acrylic glue Acrifix 192 by using a specifically developed silicone mold. The embedded membrane has the top and bottom side clear of any glue which allows exposure of the membrane to various KCl solutions. The frame made of acrylic glue allows easy handling with the membrane and attachment to the scanning cell (see Fig. 1a). Before scanning a swollen sample, we soaked the membrane in an appropriate KCl solution for at least 48 h.

2.2.2. Scanning cell

Scanning of the sample swollen in water solutions presents a significant problem due to high absorption of X-rays by water. We developed a scanning cell that allows swelling of the membrane in an appropriate water solution (Fig. 1b) and subsequently removal of the solution from the membrane by centrifugation while keeping the membrane in saturated water vapor (see Fig. 1c). This environment prevents any volumetric changes of the membrane associated with water evaporation. The scanning cell body is made of a thin walled (0.1 mm) polypropylene tube capped with tailor made CNC machined
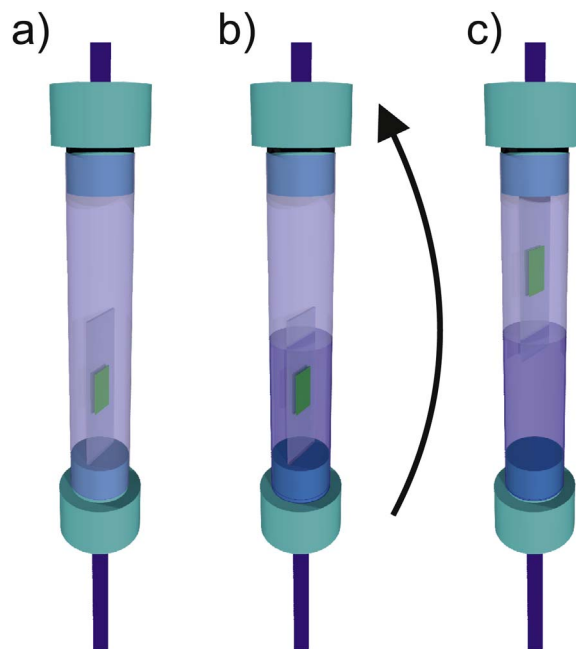
Fig. 1. Scanning cell developed for the analysis of swollen samples by μ-CT. The principle of operation is as follows: a) insertion and attachment of the sample (green rectangle represents a cut-out of the membrane) inside the cell, b) swelling the sample in a given water solution, c) turning the cell upside down (see the arrow) and removal of the remnant solution from the sample by centrifugation followed by scanning. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)