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Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Hydroxide, halide and water transport in a model anion exchange membrane



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ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form

31 March 2014

Accepted 3 April 2014

Available online 13 April 2014

Keywords:

Anion exchange membranes

Ion transport

Dissociation

Alkaline fuel cell

Diffusion

ABSTRACT

Transport of water and anions (OH^- , HCO_3^- , F^- , Cl^- , Br^- , and I^-) in a model poly(arylene ether) anion exchange membrane (AEM) with quaternary ammonium (QA) functional groups is studied for water volume fractions of $\Phi_{\text{water}} = 5\text{--}99.9\%$. At elevated water content, OH^- conductivity recorded under CO_2 free conditions occurs mainly through structural diffusion, approaching half of the H^+ conductivities of Nafion. Severe conductivity decrease at low hydration suggests incomplete dissociation of $\text{NR}_4^+ \text{OH}^-$ and inferior percolation within the aqueous domain of the AEM compared to Nafion. Further conductivity decrease result from CO_2 contamination, forming carbonates which are less mobile, less hydrated and also less dissociated from the QA compared to OH^- at a given relative humidity (RH). For other anions, conductivity decreases in the order $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ for a given RH and also for the same hydration number $\lambda = [\text{H}_2\text{O}]/[\text{QA}]$. These trends correlate with both decreasing water uptake and degree of dissociation, which is incomplete for some anions even at very high levels of hydration. Consequently, the functional groups in their halide forms display weak electrolyte behavior in contrast to the corresponding salts. Varying degrees of dissociation of different anions are held responsible for distinct variations of the nano-morphology of hydrated membranes.

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1. Introduction

Apart from separation and filtration applications [1] for which anion exchange membranes (AEMs) are well established separator materials, AEMs have the potential to be used in energy storage and conversion devices such as the alkaline polymer electrolyte fuel cell (AFC) and the redox flow battery (RFB). Currently the literature on AEMs is growing rapidly as development of AFCs with hydroxide exchange membranes (HEM) promises the use of non-noble metal catalysts as electrode material [2,3], while RFBs offer a comparatively simple way to store large amounts of electrical energy [4].

AEMs are usually made of a hydrocarbon backbone with covalently attached quaternary ammonium groups [5,6], but other functional moieties have been reported as well [7–9]. For fuel cell applications, the membrane is required to display not only good ionic conductivity but among other factors also high alkaline stability. The latter is a critical issue for any HEM since for now, they are plagued by chemical decomposition of the ammonium

moiety [10–12] and the polymer backbone itself [13], both due to nucleophilic attack by the reactive hydroxide. In the search for more durable HEMs, a plethora of different polymer backbones, functional groups, ion exchange capacities (IEC), block structures, and casting conditions have been tested, but comparison of the literature data is difficult because of varying types of experiments and conditions.

There are actually very few data on water and ion transport in AEMs though, but the notable works by Disabb-Miller [14], Hibbs [15] and Yan [16] will be considered at appropriate places in Section 3 of this paper. The fundamental understanding of transport in AEMs is still in its infancy, while transport in proton exchange membranes (PEMs) has been systematically studied for many years [17]. Nevertheless, a few characteristic similarities and differences are anticipated when comparing transport in both types of membrane.

First, transport of hydroxide (proton holes in the hydrogen bond structure of water) is not a mere mirror image of the transport of excess protons in aqueous environment space [18]. In water, both charged defects are transported, to a significant extent, by structural diffusion (commonly referred to as a Grotthuss mechanism) in addition to the vehicular process [19–21] but the rates of both processes differ by a factor of ≈ 2 (5.3 and $9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for OH^- and H^+ respectively) [22]. Speaking in terms of coordination (solvation), which plays a key role in

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structure diffusion, hydroxide is hyper-coordinated by approximately 4.5 water molecules, while excess protons are hypo-coordinated by 3 water molecules [18] with hydration enthalpies being -520 kJ/mol for OH^- and -1150 kJ/mol for H^+ [23].

Second, compared to the acidity of the superacidic sulfonic acid groups of PEMs, the quaternary ammonium hydroxide moieties in HEMs are not as strongly alkaline. Tetramethylammonium hydroxide for example precipitates below $T=40^\circ\text{C}$ in penta-hydrate form as a solid with well defined crystal structure [24,25], reminiscent of counter-ion condensation in a membrane or polyelectrolyte (especially at low water contents), when condensation of ion pairs is preferred over their dissociation and hydration in solution [26–28].

For other anions such as most halides, lower solvation enthalpies are expected to lead to even more ion condensation. This is of particular relevance for their use in redox-flow batteries in which the water activity is strongly reduced due to the presence of a high concentration of ions.

Investigating the hydroxide form for AEMs does have some difficulties which are not present with other anions or PEMs. As such, avoiding contact with ambient CO_2 is imperative, as the ensuing rapid carbonate formation can cause dramatically lower conductivities [29,30]. CO_2 also lowers the performance of HEM fuel cells as it displaces the hydroxide electrode reactions with a carbonate cycle and increases anodic over-potential [2]. This carbonate contamination is reversed under CO_2 -free conditions though, which is known as self-purging mechanism [30,31].

In this context it should also be noted that quite apart from the quest for highly conducting HEMs, there is an ongoing controversy regarding the relative alkaline stability of quaternary ammonium groups [12,32–41]. While this will not be discussed in detail here, delocalization of the positive charge alone is unlikely to stabilize a quaternary ammonium sufficiently [42], as the resulting planar geometry will decrease stability against nucleophilic attack.

In this work transport coefficients of anions (i.e. OH^- , HCO_3^- , F^- , Cl^- , Br^- and I^-) and water are presented, with data on dissociation, hydration behavior and structural correlation lengths in a model AEM. This membrane is composed of a linear, non-crosslinked poly(arylene ether) with directly attached QA groups without any side chains (experimental FuMaTech FAA-3 membrane). Samples from a single production batch were used as starting material for all experiments to ensure that they only differed with respect to the kind of anion and the water content. A non-crosslinked membrane was chosen, as this allowed one to access a very large water content range ($\Phi_{\text{water}} = 5\text{--}99.9\%$). The properties of the AEM are compared to those of the acid forms of Nafion 117 (the standard perfluorinated sulfonated acid (PFSA) membrane with long side chains) and a structurally similar sulfonated poly(ether ether ketone) (S-PEEK). The observations are discussed in terms of interdependent interactions between ions, solvent and polymer.

2. Experimental

2.1. Materials

Non cross-linked FAA-3 membrane in the bromide form was supplied by FuMaTech GmbH. Only a singular production charge (M170 011 09) was used to guarantee reproducible membrane properties. 0.02 M AgNO_3 , Na_2SO_4 , 1 M NaOH and poly(vinylalcohol) were obtained from Sigma-Aldrich, NH_3l from Merck, H_2SO_4 and NaCl from Roth.

2.2. Membrane preparation

Membranes were washed with deionized water for several days to remove all possible contaminants. To exchange the anion

they were submerged in 1 M solutions of NaCl , NaF , NH_4l or NaOH . The solution was exchanged at least three times during the course of a minimum of 48 h to ensure complete exchange. Afterwards they were washed with deionized water until the residual solution displayed equal resistance as the deionized water. The membranes were then stored in water until use. To reach higher water contents, membranes were swollen at elevated temperature and in the case of dissolved membranes, homogenized using an IKA T10 Basic Ultra-Turrax. Note that great care was taken with the hydroxide form which was prepared and measured inside a custom-made argon atmosphere glove box with a CO_2 concentration below 1 ppm at all times (ambient air 450 ppm). Samples stored inside the glove box showed no conductivity deterioration over the course of several weeks. To determine the speed and percentage of hydroxide contamination by CO_2 , Warder titration was used with a Metrohm Titrino plus 877.

2.3. Hydration behavior and ion exchange capacity

The water content was determined by weighing the membrane samples in the wet state and again after the end of the experimental run after drying in vacuo at 50°C for 24 h. The hydroxide form was converted to the chloride form (see the procedure above) before drying. To determine the IEC, membranes in the chloride form were submerged in a Na_2SO_4 solution, which was exchanged two times and then washed with deionized water. The solutions were combined, then 5 ml of a 0.2 wt% poly(vinylalcohol) solution and 5 drops of 2 M H_2SO_4 were added. This was then titrated potentiometrically using a 0.02 M AgNO_3 solution with a silver and a calomel electrode. Membranes were converted back to the chloride form before weighing. The chloride form had an IEC of 2.1 mmol/g. The IECs of other ionic forms were determined based on this value. Hydration numbers were calculated by the following formula:

$$\lambda = \frac{w_{\text{wet}} - w_{\text{dry}}}{\text{IEC} \cdot w_{\text{dry}} \cdot M_{\text{H}_2\text{O}}}$$

where w_{wet} and w_{dry} are the weight of the membrane in the wet and the dry state, respectively, IEC is the ion exchange capacity in mol/g and is the number of water molecules per functional group.

Temperature dependent water uptake was determined by submerging the membranes at the specified temperature for 2 h in water, then cooling them rapidly with cold water. Afterwards, the sample surface was quickly dried with paper towels and weighed. Water uptake at various relative humidities and temperatures were measured using a magnetically coupled scale, physically decoupled from the respective humidity and temperature. The exact setup can be found in a previous paper [43].

2.4. Conductivity measurements

A membrane column (4 mm diameter, $4\text{--}8$ mm height) was prepared by stacking a number of circular membrane pieces inside a glass cylinder and pressing them tightly together using two gold plate electrodes. This was usually done under wet conditions to ensure maximum RT hydration. The gold plate topped column was pressed between two stainless steel electrodes inside a temperature controlled cylindrical chamber using three screws for tightening. Weight and height of the stack was measured before and after each measurement to ensure water evaporation and deswelling was negligible. This allowed measurements at constant hydration. Impedance measurements were performed using an HP 4284 Precision LCR Meter (20 Hz– 1 MHz) with temperatures ranging from 25 to 65°C . Temperature measurements were calibrated using a Pt100 resistance thermometer. Conductivity

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