Bicarbonate and chloride anion transport in anion exchange membranes ☆

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ABSTRACT

Quaternary ammonium poly(sulfone) based anion exchange membrane (AEM) in Cl^- and HCO_3^- forms were characterized chemically and morphologically. It was found that the surface of the membrane in both of the forms has highly connective island-like structure, where the diameters of the hydrophilic regions are approximately 5–20 nm. Thermal gravimetric analysis of the membrane in the HCO_3^- form presented lower decomposition temperatures for the backbone and the side chains, than the membrane in the Cl^- form. In addition, the AEM in its HCO_3^- form showed higher water uptake values than in its Cl^- form across the temperature range of 25–80 °C. Conductivity experiment measured at same temperatures in both AEM forms showed higher results for Cl^- form than for HCO_3^- form. A computational model was developed in order to understand the conductivity mechanism and the relevant parameters that limit ion transport in these materials. Together with the experimental results, it was found that only 40% of the ions are free for ionic conductivity, while 60% of the ions are bound to the cationic groups, therefore unavailable to participate in the conduction process.

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1. Introduction

Recently, there has been growing interest in anion exchange membranes (AEMs) for use in electrochemical systems such as alkaline AEM fuel cells, electrolyzers and water purification devices [1,2]. AEMs generate an alkaline environment internal to the device which gives the opportunity to use platinum free [3] as well as non-precious metal catalysts for electrochemical conversion in these processes [4], substantially reducing the device costs. In addition, AEMs may be compatible with other fuels besides hydrogen [5,6], and thus relevant for a wide family of fuel cell designs.

At present, there are a few obstacles to the use of AEMs including low chemical and thermal stability in alkaline

environment [6,7]. Degradation of the chemical structure of both, side chains and the backbone, lead to deteriorated performance and short lifetime of the fuel cell. Another challenge regarding AEMs is their low ionic conductivity [8]. Hydroxide has one-half the dilute solution mobility of protons in aqueous solution, therefore, the low ion mobility is one factor in reduced conductivity of AEMs compared to proton exchange membranes [9]. Other barriers to low conductivity in AEMs are unknown, since the anion conductivity mechanism is being investigated and the complete mechanism in polymer membranes is still not clear [10].

Researchers report that hydroxide transports in AEMs is a combination of Grotthuss mechanism, diffusive transport and hopping mechanisms [11]. The Grotthuss mechanism, which is considered to be the dominant transport mechanism for hydroxide, describes hydroxide transport through AEMs by hydrogen-bonded network of water molecules (Scheme 1a [12]). The movement of the hydroxide ion is accompanied by a hyper-coordinating water molecule. The hydrated hydroxide ion is coordinated to four electron-accepting water molecules [13,14] such that when an incoming electron-donating hydrogen bond forms fully tetrahedral coordinated water molecule may be easily
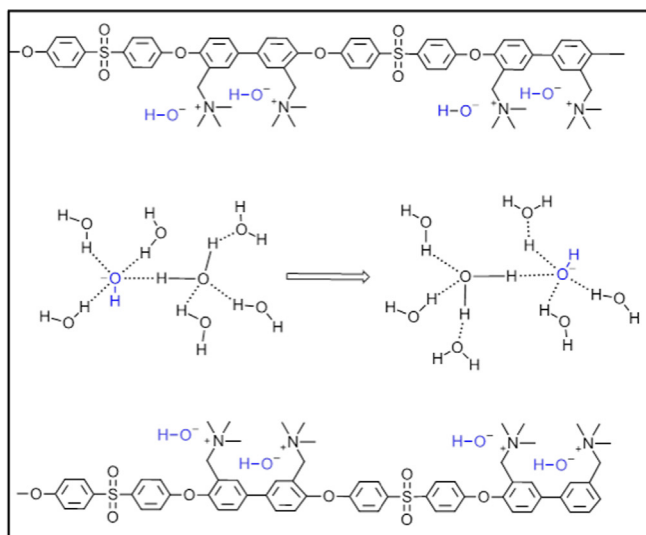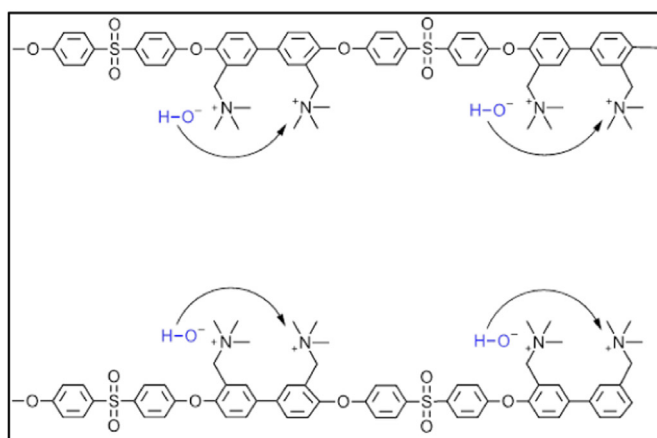
1a. Grotthuss mechanism.

1b. Surface site hopping mechanism.

Scheme 1. a. Grotthuss mechanism. b. Surface site hopping mechanism.

formed. Diffusive transport occurs in the presence of a concentration or electrical potential gradient. Surface site hopping (Scheme 1b), known as vehicular or hopping mechanism, occurs between cationic groups and recognized to be of secondary importance [11].

Investigating hydroxide transport in an alkaline AEM simulating fuel cell conditions is challenging at this stage of knowledge for two main reasons; first, hydroxide form is quickly converted to less conductive CO_3^{-2} and HCO_3^- anion forms when exposed to CO_2 and causes a mix of participate anions [9], leading to confusion in the interpretation of the results. In addition, during the experiment, hydroxide interacts with cationic groups via SN_2 and E_2 reactions [15], reducing the IEC of the membrane, thus changing their inner structure. Low humidity conditions, as present inside fuel cells, are a complex environment for ion conductivity as well. In particular, low humidity leads to partial solvation of ions or to region of non-solvated ions [16], creating a blend of hydrophobic/hydrophilic regions making analysis even more demanding.

Anions inside the membrane can be either ion-paired with the cationic side chains or free ions. Only the free ion may be transport and can therefore contribute to the conductivity. Transport of free ions inside a membrane, and thus conductivity, could be influenced by numerous parameters such as volume of hydrophilic domains through which ions are transported, tortuosity,

connectivity, steric effects, degree of ionization and ion size [17]. Phase separation and morphology are known to play key roles in fundamental properties such as ion conductivity and diffusion coefficients within the membranes.

A solution for designing highly conductive membranes is needed to identify which parameter limits the transport in AEMs. Therefore, our approach is to study AEMs in the Cl^- and HCO_3^- forms. These forms are not affected by the presence of CO_2 when the AEM is exposed to the atmosphere, and the membrane is not being chemically degraded by the attack of the anion as in the case of the AEM in the hydroxide form. The investigated counter anions, Cl^- and HCO_3, are transported via en-mass diffusion mechanism, which is well known and understood. In addition, we avoid difficulties that arise due to low humidity condition by focusing on a fully hydrated membrane. Overall, this setting is appropriate for an initial investigation of the influence of the counter ion on the basic membrane properties. The anions differ in size, chaotropic or cosmotropic nature, i.e. the influence of ions on the hydrogen bonds in water molecules, and ion-pairing tendency. These properties will allow us to identify the crucial factors for an efficient ionic transport in AEMs, while it may be even plausible that some of these factors would be relevant to hydroxide ion transport in AEMs.

2. Experimental

2.1. Polymer synthesis

Scheme, 2 shows the chemical structure of a quaternary ammonium (QA) biphenol poly(sulfone)-based AEM synthesized by chloromethylation of a commercially-available Radel polymer backbone. The AEMs in this report were synthesized using previous methods [18].

2.2. HRSEM

The membranes were cut into squares of approximately 5 mm × 5 mm and were fixed onto an aluminum stub with a double-sided conductive tape (for cross-section images, the membrane was freeze-cut). Then, the samples were sputter coated with a carbon, to improve conductivity. The observation was conducted with an acceleration voltage of 4–3 kV in a high-resolution scanning electron microscopy (HRSEM, Zeiss Ultra-Plus FE-SEM).

2.3. Ion exchange capacity (IEC)

Ion exchange capacity was measured using a potentiometric method [19]. This method enhances the accuracy of the Mohr titration method for IEC determination, especially when small quantities are measured. A membrane sample (in Cl^- form) of 30 × 30 mm², with thickness of 0.070–0.10 mm was immersed in 50 mL 0.2 M KNO_3 solution for 24 h (the solution was refreshed 3 times) and titrated with 0.02–0.1 M $AgNO_3$. The IEC was

R = H or $CH_2N^+(CH_3)_3OH^-$
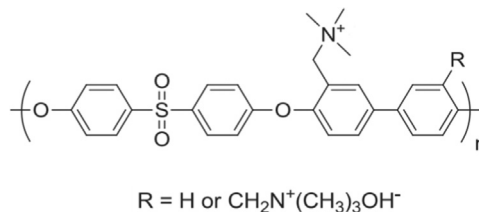
Scheme 2. Chemical structures of quaternary ammonium functionalized poly (sulfone) anion exchange membrane.