Hydroxide-ion induced degradation pathway for dimethylimidazolium groups in anion exchange membranes

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ARTICLE INFO

ABSTRACT

The alkaline stability of imidazolium-based anion exchange membranes was studied by FT-IR and ^{13}C solid state NMR. Imidazolium groups are susceptible to attack by hydroxide ions and undergo degradation in alkaline conditions through a ring-opening mechanism. Density functional theory (DFT) studies were performed to better understand the degradation pathway and the relative stability of imidazolium cations on exposure to hydroxide. The ring-opening degradation pathway follows the following three steps: (a) a nucleophilic reaction, (b) a ring-opening reaction, and (c) a rearrangement reaction. The structural changes induced in the imidazole ring were studied using a model of the dimethylimidazolium cation ([DMIM]$^+$). The energy changes along the degradation pathway were obtained from reaction path calculations. The effect of hydroxide ion concentration and dielectric constant of surrounding medium on reaction energy barriers were studied. The hydroxide-ion induced degradation of the dimethylimidazolium cation was found to be more facile in high-pH environments. Good solvation of the dimethylimidazolium cation and the hydroxide ion was helpful in minimizing the degradation and enhancing the chemical stability of anion exchange membranes based on these cations.

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1. Introduction

Anion exchange membrane fuel cells (AEMFCs) are a class of fuel cells that operate at temperatures < 100 °C using a solid anion exchange membrane (AEM) electrolyte in place of the aqueous KOH electrolyte used in traditional alkaline fuel cells (AFCs). AEMFCs have the potential to be used for both vehicular and portable applications, though the latter application is more likely in the shorter term [1,2]. Solid alkaline electrolyzers also pose an attractive proposition for efficient hydrogen generation [3–5]. Alkaline electrolytes allow for the use of non-precious-metal catalysts such as Fe/Co/Ni and non-carbon supports [6–9] to facilitate the electrochemical reduction/evolution of oxygen. Recently, non-precious-metal-based catalysts for the hydrogen oxidation/evolution reaction have also been unearthed [10–12].

Although the ionic conductivity of AEMs is highly sensitive to membrane hydration levels when compared to proton exchange membranes (larger decrease in conductivity with reduced hydration levels), the ionic conductivity of AEMs is not the only factor limiting AEMFC performance [13–15]. A known issue with current AEMs is their chemical instability under alkaline conditions. We have studied both backbone and cation degradation in AEMs in alkaline and acidic environments and have probed the stability of AEMs using multi-dimensional NMR methods [16–21]. Prior evidence in the literature [1,22,23] shows that the chemical stability of functional cationic groups (such as tetraalkylammonium and imidazolium cations) is inadequate for long-term application in AEMFCs. The identification of functional cationic groups with acceptable chemical stability should therefore be a key research priority. The thermal stability and ionic conductivity at lower water uptakes (corresponding to minimal AEMs swelling) should also be considered while designing AEMs. Some of the functional cationic groups reported in the literature thus far include quaternary ammonium [24–26], quaternary phosphonium [27], organometallic [28], imidazolium [29–32], and guanidinium [33–35].

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Recently, there has been much interest on the topic of imidazolium-based AEMs for application in AEMFCs [36–38]. Unfortunately, imidazolium cations tend to undergo ring-opening degradation at higher pH and thereby lose the ability to transport anions. In this paper, the alkaline stability of imidazolium based AEMs was studied by monitoring IEC and hydroxide ion conductivity, and by using FT-IR and ^{13}C solid state NMR. We also discuss and report the hydroxide-ion induced degradation pathway for the dimethylimidazolium cation using density functional theory (DFT) calculations. The influence of OH^- concentration and the effect of solvation on the stability of dimethylimidazolium cations are discussed.

2. Experimental

2.1. Materials

Fluorinated poly (aryl ether oxadiazole) AEMs derivatized with imidazolium cations (FPAEO-2.2 MIM, 2.2 refers to the theoretical molar ratio of 1-methylimidazole to FPAEOM) were prepared as described in reference [30] and shown in Scheme 1.

2.2. Membrane characterizations

#### 2.2.1. Ion exchange capacity (IEC) and hydroxide ion conductivity (σ)

IEC was measured as previously reported [30]. The accurately weighed sample was converted to its Cl^- form by immersing in 0.5 mol L^{-1} NaCl solution for 48 h at 25 °C. Then the sample was washed with deionized water to remove the excess NaCl and immersed in fixed volume of 0.1 mol L^{-1} NaNO$_3$ solution for 24 h. The amount of replaced Cl^- was determined by titration with 0.05 mol L^{-1} AgNO$_3$ solution using $K_2Cr_2O_7$ (10%) as an indicator. The IEC value was calculated according to the following equation:

$$IEC \ (m \ mol \times g^{-1}) = \frac{0.05 \times V_{AgNO_3}}{W_d} \qquad (1)$$

where V_{AgNO3} (mL) is the volume of the AgNO$_3$ solution, and W_d (g) is the weight of the dried membrane sample.

Hydroxide ion conductivity of the sample was measured via the two-point probe electrochemical impedance spectroscopy (EIS) technique using a Zahner IM6ex electrochemical working station with an AC perturbation of 10 mV and over the frequency range 100 Hz to 3 MHz [30]. The membrane was immersed in deionized water for 24 h before testing. The membrane was clamped between two Pt electrodes using two Teflon® blocks, placed in deionized water at 25 °C and evaluated. The hydroxide ion conductivity (σ) of the membrane was calculated according to the following equation:

$$\sigma \ (S/cm) = \frac{L}{R \times S} \qquad (2)$$
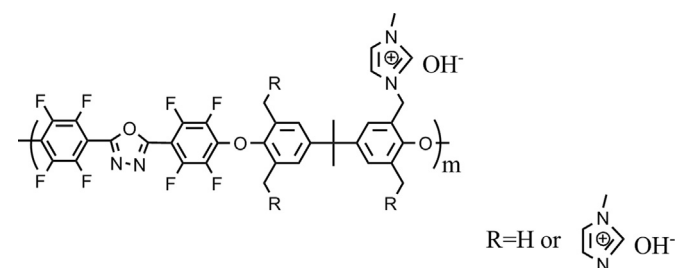
where L (cm) is the distance between two Pt electrodes, R (Ω) is the real impedance corresponding to zero phase angle in the impedance spectrum, and S (cm^2) is the cross-sectional area of the membrane orthogonal to l.

2.2.2. FTIR and solid state ^{13}C NMR

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet Magna 750 Fourier transform infrared spectrometer. ^{13}C solid state NMR spectra (cross polarization, magic-angle spinning) were recorded on a Bruker AV300 spectrometer using tetramethyl-silane (TMS) as the internal standard. Measurements were carried out at ambient temperature and pressure, and the samples were air-dried before measurement.

2.2.3. Alkaline stability

To investigate the alkaline stability of imidazolium based AEMs, the membrane was treated with 1 mol L^{-1} and 5 mol L^{-1} NaOH aqueous solutions at 25 °C for 5 days, respectively. The values of IEC and hydroxide conductivity of the membranes before and after the alkaline treatment were measured.

2.3. Computational details

The optimized geometries and calculated energies of all species reported in this paper were obtained with B3LYP DFT and 6–311++g (d, p) basis set, as implemented in Gaussian 09 (G09) software [39]. During the calculations, a polarizable continuum solvation model (PCM) in G09 was used to account for the water medium surrounding the species. The force constants were conveniently computed based on the optimized structure, resulting in the thermodynamic free energies (G) and vibrational frequencies. For a reaction $A+B \rightarrow [AB]^{\neq} \rightarrow C$, we optimized the geometries of species A, B, and C in water medium. At the same time, the geometry of the transition state $[AB]^{\neq}$ was obtained from this approximate point by using the Berny optimization algorithm as implemented in G09. Subsequently, the standard free energy change for that reaction was defined as $\Delta G^0 = G^0(C) - (G^0(A) + G^0(B))$. The activation free energy barrier for that reaction was defined as $\Delta G^{\neq,0} = G^0([AB]^{\neq}) - (G^0(A) + G^0(B))$. The simulations were carried out corresponding to a temperature of 298.15 K and a standard pressure of 101.325 kPa. All optimized geometries (and reported data) were based on counterpoise-corrected optimized geometries.
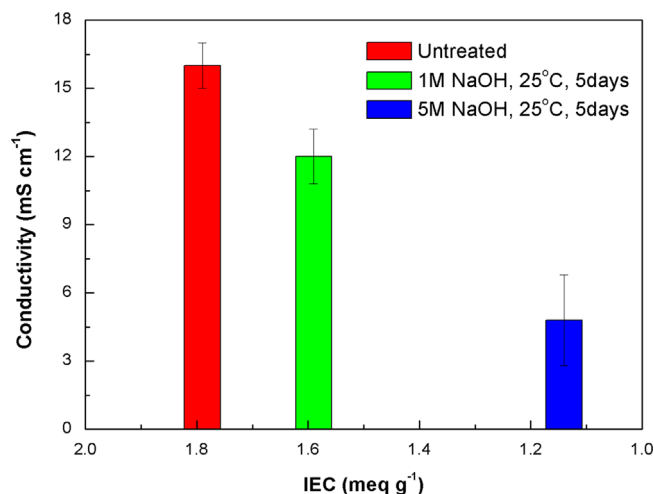

Fig. 1. IEC and hydroxide ion conductivity of FPAEO-2.2 MIM membranes before and after treatment in 1 and 5 mol L^{-1} NaOH aqueous solutions at 25 °C for 5 days.

Scheme 1. Fluorinated poly(aryl ether oxadiazole) AEMs derivatized with imidazolium cations (FPAEO-2.2 MIM, 2.2 refers to the theoretical molar ratio of 1-methylimidazole to FPAEOM).