Infrared spectroscopy of ion-induced cross-linked sulfonated poly(ether ether ketone)

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ABSTRACT

The dehydration of SPEEK-[H] (protonated sulfonated poly(ether ether ketone)) converts 3-fold symmetric (C_{3V}) hydrated sulfonate sites to sulfonic acid sites with no local symmetry (C_1). Like Nafion-[H], SPEEK-[H] C_{3V} and C_1 environments afford IR group modes ($C_{3V,HF}$ (1087 cm^{-1}); $C_{3V,LF}$ (1026 cm^{-1}) and $C_{1,HF}$ (1362 cm^{-1}); $C_{1,LF}$ (904 cm^{-1})) due to the mechanical coupling of vibrational internal coordinates of an ether link with those of the sulfonate or sulfonic acid exchange site. C_{3V} and C_1 bands are inversely correlated during membrane hydration/dehydration. Hydrated SPEEK-[M] (M: Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Sr^{2+} or Ba^{2+}) exhibits SPEEK-[H] C_{3V} bands because cation waters of hydration preclude binding to the hydrated exchange site. When cation hydration spheres are thermally stripped at high vacuum, SPEEK-[M] C_{3V} bands supplant SPEEK-[H] C_{3V} bands, inducing SPEEK cross-linking. Incomplete cross-linking is evidenced by low intensities of SPEEK-[M] $C_{1,HF}$ bands. The 1362 cm^{-1} band intensities are inversely correlated with cation hydration enthalpies.

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1. Introduction

Nafion and sulfonated poly(ether ether ketone) (SPEEK) membranes (Fig. 1) are ideal for polymer electrolyte membrane (PEM) fuel cells because of the high proton conductivity afforded by sulfonate exchange groups ($-SO_3^-$) and their robust backbone structures [1–3]. Nafion, a perfluorinated carbon backbone with vibrationally hinged (ether link) side chains that terminate with a sulfonate exchange site, has been the dominant PEM fuel cell electrolyte for several decades [4–6]. Although Nafion has excellent chemical stability and proton conductivity [4], it is expensive, has diminished conductivity above 90 °C [4,7,8], is subject to a free radical catalyzed unzipping mechanism [3] and generates fluorinated toxins when incinerated [9,10]. SPEEK is lower cost, has high chemical, thermal, and mechanical stability [1,7,11], and is environmentally friendly [12,2,3,13,14].

Differences in morphology and microstructure account for functional discrepancies (e.g., proton conductivity, thermal stability) between SPEEK and Nafion [15]. SPEEK has narrower aqueous channels and dead ended aqueous confines that result in lower proton conductivity than Nafion with the same degree of sulfonation [3,15]. While proton conductivity increases with degree of sulfonation [14,16,17], membrane swelling also increases, diminishing mechanical strength [1,2,12,13,15,11,18–20]. Cross-linking mitigates much of the mechanical limitations imposed by higher degrees of sulfonation [8,13,11,18,20] to the extent that highly sulfonated cross-linked SPEEK can outperform Nafion [21,22]. Unfortunately the benefits of cross-linking [8,13,19–23] come at the expense of lower proton conductivity [19].

SPEEK cross-linking methods are not well developed due to the rigid backbone structure. SPEEK ether links are hampered vibrational hinges because their lone pair electrons are delocalized by resonance. While most cross-linking strategies involve covalent bonding, ionic bonding [8] and a combination of both [20] have been explored. Chemical (covalent) cross-linking [22,24] is done through electron beam irradiation [11], UV irradiation [23], free radical reactions or the use of PEEK precursors that generate cross-linked products [8]. Physical methods are less understood [22], but provide facile methods for study of cross-linking. Ionic cross-linking is a physical method that requires the maintenance of electrical neutrality [22]. Narducci et al. suggest ionic cross-linking by divalent ions in hydrated SPEEK membranes [25]. Cross-linking
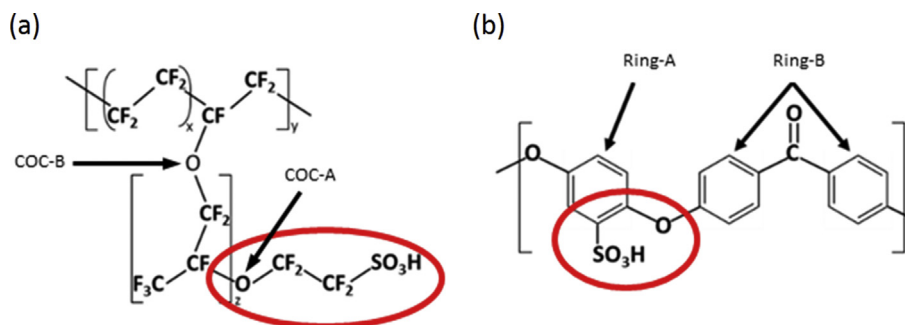
Fig. 1. Chemical repeat units of (a) Nafion and (b) SPEEK. The proximity of the ion exchange site to an ether link [34] (circled in red) is common to both structures.

with Sr^{2+} and Ba^{2+} has been reported [8,22]. Quezado et al. conducted a comprehensive FTIR study of metal ion-water interactions in Nafion at low levels of hydration [26]. Their study of 20 cations at wavenumbers above 1550 cm^{-1} showed that Lewis acid and base strengths of cations and anions are good indicators of their affinity for each other and of the resistance of cation-anion pairs to disruption by water molecules. Our recent report on interactions between cations and the exchange group, in totally dehydrated Nafion, focused on wavenumbers below 1200 cm^{-1}: Strong binding between cations and the dehydrated exchange group feature C_{3V} local symmetry with substantial orbital overlap between the metal ion and the exchange site sulfur atom [27]. Our crystal orbital overlap population calculations also showed a surprisingly high level of orbital overlap between lithium and the exchange site sulfur [27]. This explains why lithium-exchanged sulfonated ionomers are not good battery electrolytes [28,29]. Quezado et al. also reported anomalously strong interactions between Li$^+$ and Nafion exchange sites [26].

The proximity of the exchange site to an ether link (Fig. 1, red circles) yields striking similarities between Nafion and SPEEK vibrational spectroscopy. They both have IR group modes derived from the mechanical coupling of the exchange site with a nearest neighbor ether link (e.g., COC-A in the case of Nafion) [30]. These IR group modes are categorized in terms of the local symmetry of the exchange site, which depends on the state-of-hydration and the charge compensating ion [3,27,30—33]. When the membrane is hydrated, the exchange site is dissociated to the sulfonate form and has a C_{3V} local symmetry. At lower states-of-hydration the exchange site associates to a sulfonic acid form that has no local symmetry (i.e. C_1). Thus group modes that are consequences of the mechanical coupling of the exchange site to the nearest neighbor ether link are categorized as either C_{3V} or C_1 group modes.

In Nafion-[H], the higher frequency C_{3V} mode (1060 cm^{-1}), referred to as $C_{3V,HF}$, is dominated by COC-A motions that are mechanically coupled to the exchange site. The $C_{3V,LF}$ (969 cm^{-1}) is dominated by exchange site motions coupled to a smaller COC-A contribution [30—32]. Proton association during dehydration of Nafion-[H] yields the sulfonic acid form of the exchange site ($-SO_3H$) which has no local symmetry (C_1) [3]. This gives rise to Nafion $C_{1,HF}$ (1414 cm^{-1}) and $C_{1,LF}$ (910 cm^{-1}) group modes, derived from the mechanically coupled internal coordinates of COC-A and the $-SO_3H$ exchange site [27].

The assignment of IR bands attributed to the side chain of hydrated Nafion in terms of a single functional group has led to enormous confusion [30,35—37]. For example, the 1060 cm^{-1} is frequently assigned as a $-SO_3^{-1}$ mode. Similarly, the 969 cm^{-1} is assigned as a COC-A mode [30,35,36]. These single functional group assignments preclude understanding of why their band intensities are strongly and inversely correlated to alterations of the exchange

site environment [3,27,30—32]. The assignment of these Nafion bands as local symmetry based *group* modes is paradigm shift from decades of history: The 1060 cm^{-1} and 969 cm^{-1} bands are COC-A, $-SO_3^{-1}$ and COC-A, $-SO_3^{-1}$ group modes respectively. Both modes are attributed to the same mechanically coupled functional groups, which are listed in order of importance in their respective assignments. The primary functional group contributors, in both modes, are the reverse of the historical assignments [3,27,30,31,38,39].

Proton and metal ion exchanged Nafion membranes are designated as Nafion-[H] and Nafion-[M], respectively [27]. At high states-of-hydration the Nafion-[M] sulfonate exchange site environment is spectroscopically indistinguishable from that of Nafion-[H] because cation waters of hydration preclude direct binding of the cations to the exchange site.

The correlations of ionomer exchange site local symmetry, state-of-hydration, and ion-exchange, to density functional theory (DFT) calculated normal modes and observed IR bands would be better understood and reinforced if extended to other sulfonated ionomers [3,30—32,38,40]. This work establishes symmetry-based IR group mode assignments for SPEEK-[H] and applies them towards the analysis of dehydrated SPEEK-[M], where M is Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Sr^{2+} or Ba^{2+}.

2. Experimental

2.1. Ion exchange

SPEEK Fumapem-E- 730 (Fumatech, Bietigheim-Bissingen, Germany) membranes were used as is and soaked in 1 M salt solutions ($CdCl_2$, $CuSO_4$, $NiCl_2$, $Pb(NO_3)_2$, $Ba(C_2H_3O_2)_2$ and $Sr(C_2H_3O_2)_2$) (48 h).

2.2. Membrane transmission FTIR spectroscopy

SPEEK membranes were removed from solution, briefly rinsed with Nanopure™ water, pat-dried with ChemWipes™, and placed in the Vertex 70 FT-IR spectrometer (Bruker, Billerica, MA) to obtain the spectra of the fully hydrated membrane under ambient conditions. The sample is then transferred into the Vertex 80 vacuum (1.00 hPa) spectrometer (Bruker, Billerica, MA), enclosed within a custom glovebox, for time dependent spectra [3]. Spectra were obtained every half hour for one full day, and then hourly until a steady state condition was attained (12—60 h). Dehydration was continued on a high vacuum line (60 °C, 2 days) equipped with a Welch 1402 DuoSeal vacuum pump, a glass oil diffusion pump (Ace Glass, Vineland, NJ) and a liquid N_2 trap. After dehydration, the sample bulb was transferred to the FT-IR glove box, and the membrane returned to the Vertex 80 sample chamber for acquisition of a final spectrum. Spectra were signal averaged (50 scans,