



# Theoretical and experimental infrared spectra of hydrated and dehydrated sulfonated poly(ether ether ketone)



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## ABSTRACT

Time-dependent FT-IR spectra of sulfonated poly(ether ether ketone) during dehydration show diminishing 1081  $\text{cm}^{-1}$  and 1023  $\text{cm}^{-1}$  band intensities concurrent with the emergence and shifting of bands at 1362  $\text{cm}^{-1}$  and 898  $\text{cm}^{-1}$ . Animations of density functional theory calculated normal modes enable assignment of the 1081  $\text{cm}^{-1}$  and 1023  $\text{cm}^{-1}$  bands as group modes that include a sulfonate exchange site with  $C_{3v}$  local symmetry, while the 1362  $\text{cm}^{-1}$  and 898  $\text{cm}^{-1}$  bands are assigned as group modes that include an associated sulfonic acid with no local symmetry ( $C_1$ ). In contrast to analogously assigned Nafion group mode bands, the SPEEK  $C_{3v}$  and  $C_1$  bands coexist throughout the entire dehydration–hydration cycle, suggesting the presence of associated and dissociated exchange sites in SPEEK at all states-of-hydration. This supports a morphological model for SPEEK featuring branched hydrophilic domains and dead-end aqueous confines.

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## 1. Introduction

Perfluorinated sulfonated polymer electrolytes, such as Nafion (Fig. 1, left), are widely used in fuel cells because of their high proton conductivity and perceived chemical stability [1–5]. However, such membranes are expensive and rapidly diminish in conductivity at temperatures above 90 °C. Perfluorinated polymers are not environmentally friendly. Polymer electrolyte membranes are often coated with expensive catalysts (e.g., Pt, Ru, Ir, etc.). The recovery of catalysts requires incineration of the membrane electrode assembly, yielding toxic emissions (HF,  $\text{C}_2\text{F}_4$ , and other fluorocarbons) [6,7] which must be scrubbed before release into the atmosphere. Nafion undergoes radical decomposition, otherwise known as “unzipping”. Hydroxide radicals formed at the fuel cell anode cause the radical decarboxylation of Nafion at the backbone terminal to yield a  $-\text{CF}_2$ -radical [7–10]. The radical degradation process continues through the intermediates of  $-\text{CF}_2\text{OH}$  and  $-\text{COF}$ , finally regenerating  $-\text{CF}_2\text{-COOH}$  with one less carbon. This

unzipping cycle continues while releasing HF and carbon dioxide. Schematic of the Nafion radical degradation process can be found in the [Supplementary Material](#).

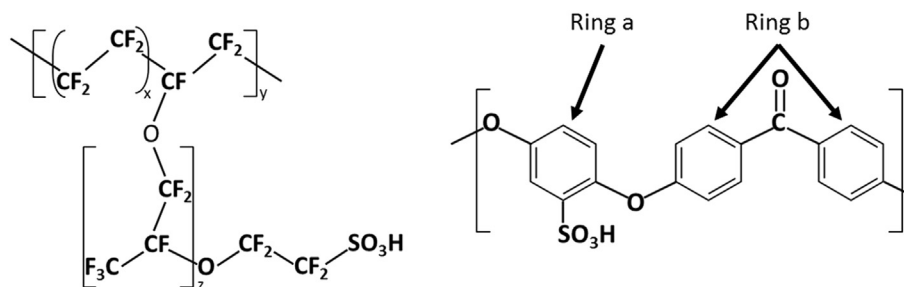
Sulfonated polyaromatic membranes, for example sulfonated poly(ether ether ketone), are substantially less expensive to prepare, and have phenolate terminal end groups that have not been reported to contribute to a radical unzipping mechanism [11–16]. The hydrocarbon-based structure of SPEEK (Fig. 1, right) lends itself to catalyst recovery with less environmental impact upon incineration. Thus SPEEK or similar hydrocarbon membranes may supplant Nafion for catalyst coated membranes [17–20].

The Gierke and Hsu Nafion sphere-and-cylinder model [21,22] has been improved upon by models incorporating transitional interphases [23,24] that separate the hydrophilic (ion-exchange group) and hydrophobic (backbone) domains. For example, the Yeager and Steck three-phase model [25] contains aqueous confines with no specific geometrical definition and transitional interphases with substantially lower degrees of order than Gierke's spheres and cylinders. Other models include a core–shell structure [26], a lamellar model [27], a sandwich-like model [28] and local order models [29,30]. Mauritz and Moore [23], after extensive review of the state of understanding of Nafion, conclude that at least three phases (hydrophilic, hydrophobic, and a “fuzzy” interphase)

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**Fig. 1.** LEFT: Nafion chemical repeat unit. RIGHT: SPEEK repeat unit. The proximity of the ion exchange group to an ether link is common to both structures. Both structures are vibrationally hinged by ether linkages.

exist, incorporating an extended aqueous phase in hydrated membranes.

Kreuer et al. [4] contrast the morphology of SPEEK with that of Nafion. The narrower channels and dead end pockets of SPEEK decrease proton conductivity at high temperatures and/or low states of hydration [31]. While higher degrees of sulfonation increase the water uptake [32], the lower equivalent weight decreases ionomer mechanical stability [33]. A fundamental understanding of the relationships between degree of sulfonation, water uptake and mechanical stability would facilitate development of better polymer electrolytes. The establishment of infrared (IR) spectroscopy as a powerful method for study of water in ionomers [34–36] motivated our work to correlate time-dependent IR spectroscopy of dehydrating Nafion to density functional theory (DFT) calculated normal mode analysis [37–39].

DFT-calculated vibrational normal mode analysis requires selection of a structural model. In our previous work [38,39], a 55-atom Nafion chemical repeat unit was selected. A more realistic choice would have been a physical repeat unit, which contains geometric irregularities and macroformations that cannot be represented by a chemical repeat unit [40]. However, the high level of theory required for DFT-calculated normal mode analysis precludes the use of a complex physical repeat unit. As a compromise, we use an 86-atom SPEEK fragment (two 37-atom chemical repeat units plus an additional aromatic ring (Fig. 2, left)). The molecular dynamics-calculated morphology of hydrated SPEEK by Brunello [41] is shown (Fig. 2, right).

At high states-of-hydration, the dissociated super acidic exchange site [42] is in the form of sulfonate, which has a local 3-fold axis of symmetry (i.e.,  $C_{3V}$ ). At low states-of-hydration, the associated sulfonic acid form has no local symmetry (i.e.,  $C_1$ ). During rigorous dehydration of Nafion, the  $C_{3V}$  modes vanish while  $C_1$

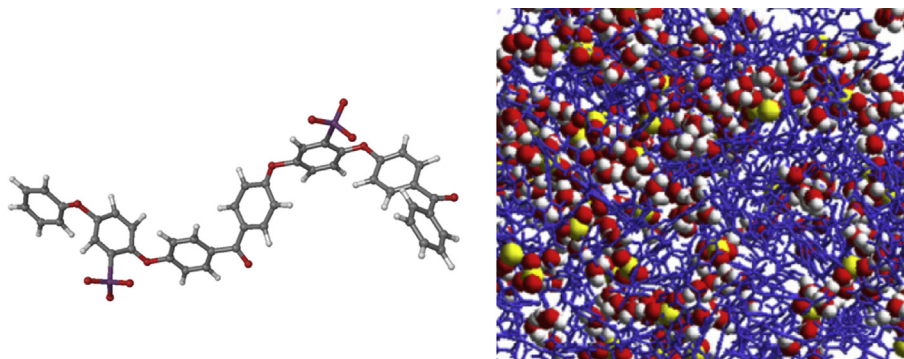
group modes emerge concomitant with association of the exchange sites with protons. We augmented time-dependent FTIR spectroscopy with DFT calculations to correlate Nafion group modes (sensitive state-of-hydration) to motional contributions from the ion-exchange side chain atoms [38,39]. The state-of-hydration ( $\lambda = \text{water/exchange-site}$ ) does not vary linearly with time. We are now correlating the Nafion state-of-hydration to the intensity of selected  $C_{1V}$  group modes to elucidate the functional relationship between time and  $\lambda$  during dehydration.

The exchange site local symmetry basis for assignment of group modes is applicable to SPEEK, which has a sulfonic acid group beta to an ether link, as does Nafion. The application of this theory-experiment methodology to ionomers in general will advance our understanding of the relationship between state-of-hydration and the morphology of polymer electrolytes.

## 2. Experimental

### 2.1. Preparation of SPEEK membrane

[43,44] PEEK (Victrex 450P) was sulfonated by reaction with concentrated sulfuric acid (96–98%) under nitrogen (50 °C, 48 h). The product was precipitated in ice-cold water with constant stirring. The precipitate was settled overnight, filtered and washed several times with water, using a dialysis membrane (Sigma–Aldrich D9402) to remove sulfuric acid and attain neutral pH. The resulting SPEEK was dried overnight (80 °C). Casting solvents were prepared by dissolving SPEEK in dimethyl sulfoxide (200 mg into 6 mL) and evaporating down to half the volume (3 mL) at 90 °C. The solution was cast onto a Petri dish and dried for 24 h at 120 °C, resulting in a membrane.



**Fig. 2.** LEFT: SPEEK fragment DFT model RIGHT: SPEEK physical microstructure (10 wt. water) simulated through molecular dynamics. PEEK backbone chain is depicted in blue (includes carbonyl and ether group oxygens), sulfur atoms in yellow, sulfonate and water oxygens in red, and hydrogen in white. Image reproduced with permission from Brunello [41]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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