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Direct ESR detection and spin trapping of radicals generated by reaction of oxygen radicals with sulfonated poly(ether ether ketone) (SPEEK) membranes

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ABSTRACT

The stability of membranes under the strong oxidizing conditions in fuel cells is one of the major challenges in the development of fuel cells based on proton exchange membranes (PEMs). This study is centered on the determination of the susceptibility to degradation of SPEEK membranes exposed to •OH radicals, using both direct ESR and spin trapping with 5,5-dimethyl-1-pyrroline-1-oxide (DMPO). In order to achieve a complete picture on SPEEK degradation, two types of experiments were performed: 1. UV irradiation at 77 K of SPEEK membranes swollen by aqueous solutions of H_2O_2; 2. UV irradiation of SPEEK membranes swollen by aqueous solutions of H_2O_2 in the presence of DMPO as a spin trap. UV irradiation without oxygen of SPEEK at 77 K in acid or basic form in the presence of H_2O_2/H_2O produced phenoxyl radicals as the predominant radicals detected by direct ESR or spin trapping methods. At pH 4, the oxygen radicals produced phenyl radicals as the predominant species detected by spin trapping methods. The hydroperoxyl radical, as DMPO/OOH adduct, was detected only when the DMPO/OH adduct was absent. The appearance of phenyl and phenoxyl radicals provides the evidence that •OH radicals react with the aromatic ring of SPEEK or leading to the scission of its ether bridge.

1. Introduction

Sulfonated poly(aryletherketone) membranes have been developed for use in hydrogen and direct methanol fuel cells (DMFCs). The most commonly used membranes have an ether–ether–ketone sequence, EEK, as in the case of sulfonated poly(ether ether ketone) (SPEEK) membranes. Reaction of PEEK with sulphuric acid leads to sulfonation of the O-phenyl-O units (Structure 1) and to membranes with a broad range of solubilities, conductivities, mechanical properties, and degree of swelling by solvents [1–8]. The degree of sulfonation (DS) dictates the solubility of the membrane: for DS>30%, SPEEK ionomers are soluble in dimethylformamide (DMF), dimethylsulfoxide (DMSO), and N-methylpyrrolidone (NMP); solubility in methanol occurs in membranes for DS>70%; and in hot water for DS ≈ 100% [1,3]. The advantages of using SPEEK membranes in DMFCs are reduced swelling by methanol when compared to Nafion membranes as a reference, reduced methanol crossover, and improved electrode kinetics [1,2,4,5].

The reactions of •OH radicals with aromatic compounds showed that the addition of •OH radical to the phenyl ring is more favorable than that of hydrogen abstraction, giving a cyclohexadienyl type radicals due to the combined ortho- or para-activation to alkyl- (R-) or RO-substituents and the meta directing effect of SO_3 group (arrows in Structure 1) [8]. In addition, the pH can have an important effect on the type of radicals. Furthermore, these radicals could be studied by ESR methods.

Spin trapping is an analytical technique employed in the detection and identification of short-lived free radicals. Spin trapping involves the addition of radical to a nitrone spin trap resulting in the formation of a spin adduct, a nitroxide-based persistent radical, that can be detected using electron spin resonance (ESR) spectroscopy. The spin adduct usually yields a distinctive ESR spectrum characteristic of a particular free radical that is trapped.

Electron spin resonance (ESR) methods are used in our laboratory for the study of stability and degradation processes in PEMs, because this technique is sensitive and specific for the detection of radical species [9–13]. In the laboratory, oxygen radicals can be generated by two major methods: (a) The Fenton reagent, where

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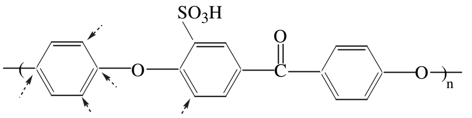

Structure 1. Chemical structure of SPEEK; arrows represent the favorable positions where the oxygen radicals can attack the phenyl rings due to the combined effects of ortho-, para- activation to alkyl- (R-) or RO-substituents and the meta directing effect of SO_3H function.

the major step is $H_2O_2 + Fe(II) \rightarrow Fe(III) + {}^\bullet OH + HO^-$ [14]. (b) Photolysis of aqueous solutions of H_2O_2, and the main expected reactions are [15]:

$$H_2O_2 \rightarrow 2{}^\bullet OH \tag{1}$$

$$^\bullet OH + H_2O_2 \rightarrow {}^\bullet OOH + H_2O \tag{2}$$

$$^\bullet OH + H_2O \rightarrow O_2{}^\bullet - + H_3O^+ \tag{3}$$

The formation of radical species from the attacked substrate, for example R•, can occur by H-abstraction, $^\bullet OH + RH \rightarrow H_2O + R^\bullet$; the polymer-derived R• radicals can initiate a degradation cascade.

The presence of the oxygen radicals was confirmed in our laboratory by direct ESR, using a combination of UV irradiation and ESR measurements at low temperature, typically 77 K, followed by gradual annealing of irradiated samples for short intervals (≈3 min) above 77 K. In this way ESR signals from the •OH, •OOH and $O_2{}^\bullet-$ radicals have been detected [15].

We present a study of SPEEK membranes exposed to oxygen radicals generated by UV irradiation of aqueous solutions of H_2O_2. As will be seen below, the presence of radicals was detected by direct ESR; additional details on the type and relative intensity of the various radical species were obtained by spin trapping with 5,5-dimethyl-1-pyrroline-1-oxide (DMPO). In most cases the ESR spectra of spin adducts exhibit hyperfine splittings (hfs) from the ^{14}N and H_β nuclei. Spin trapping is based on scavenging of short-lived radicals by spin traps and formation of more stable adducts, typically nitroxide radicals [16–21]. The DMPO as spin trap was chosen because the hfs of the DMPO adducts are sensitive to the nature of the trapped radicals R• [22]; moreover, DMPO was used extensively for the detection of oxygen radicals such as •OH, •OOH and $O_2{}^\bullet-$, as well as carbon-centered radicals (CCRs) [11,12,18–36]. The clear distinction between these two groups of free radical adducts is based on the large difference in the hfs of the H_β protons: typically 10–15 G for oxygen adducts, and >20 G for carbon-centered radical adducts, respectively. Spin trapping by DMPO is often complicated by the presence of two types of radicals directly derived from the spin trap: the product of DMPO oxidation, 5,5-dimethyl-2-oxopyrroline-1-oxyl (DMPOX) with $a_N = 7.2$ G and $a_{H\gamma} = 4.2$ G (two protons) [11,20,27,32], and the radical formed by cleavage of the N–C bond and ring opening, with $a_N \approx 15$ G [28]. In the presence of more than one radical, the selectivity of the spin trap is also an important issue.

In a recent paper the kinetics of trapping ethanol-derived radicals and •OH radicals was compared [23]. The goal in the spin trapping experiments is to translate these splittings into an identity of a radical. The spin trapping data base is a useful resource [37].

It should be mentioned that the hfs (a_N, $a_{H\beta}$ or $a_{H\gamma}$) of DMPO adducts can be slightly different for a given adduct, due to the local polarity or the conformation of spin trap adduct [22,23,37].

The goal of our experiments was to study the behavior in presence of oxygen radicals of a membrane that is known to have low chemical stability (SPEEK), and to compare it with the behavior of Nafion as a reference, which has been studied in our laboratory by exposure to the Fenton reagent, and by UV irradiation of H_2O_2 in the presence of Fe(II), Fe(III), and Cu(II) counterions [10,11,13].

2. Experimental section

2.1. Materials

The SPEEK membrane (2 meq sulfonic groups/g) was a gift from T. Fuller of the GM Fuel Cell Center in Honeoye Falls, NY, and was prepared by sulfonation of PEEK from ICI by Scientific Polymer Products, Ontario, NY. Solutions of SPEEK in dimethylacetamide (18% by weight) were cast on a glass plate and dried in air for 16 h and at 80 °C for at least 1 h. The coated film was released from the glass plate by immersion in water, and the free-standing film was then allowed to dry in air. Prior to the ESR experiments, the membrane was dried under vacuum for 24 h at 35 °C. The DMPO as the spin trap (99.97%) was purchased from Aldrich–Sigma Chemical Company and used without further purification. Dimethylsulfoxide (DMSO, 99.9%) from Aldrich–Sigma Chemical Company, the buffer solution from Orion Research, and hydrogen peroxide (3% w/v) from Fisher were used as received.

2.2. Sample preparation

Samples were prepared from deionized and double distilled water (or buffer solution) and H_2O_2, and dried membrane pieces of typical size 5 × 15 mm^2. The dry membrane was soaked in the ESR sample tube for 4 h with the H_2O_2 solution in the refrigerator to prevent H_2O_2 decomposition; the supernatant was then removed, and the samples were immersed in liquid nitrogen prior to UV irradiation at 77 K. For the spin trapping experiments, the DMPO solution in the appropriate solvent was added prior to or after irradiation. Fully neutralized membranes were prepared by immersion in KOH aqueous solution for 24 h, followed by drying in the ESR sample tube for 24 h at 30–35 °C under vacuum.

When the irradiation was performed on membrane solutions, samples consisting of SPEEK dissolved in DMSO (or $DMSO_{d6}$) (1% w/v), aqueous solution of H_2O_2 (3% w/v), and DMPO solution in appropriate solvent were bubbled with nitrogen for 5–10 min. The concentrations

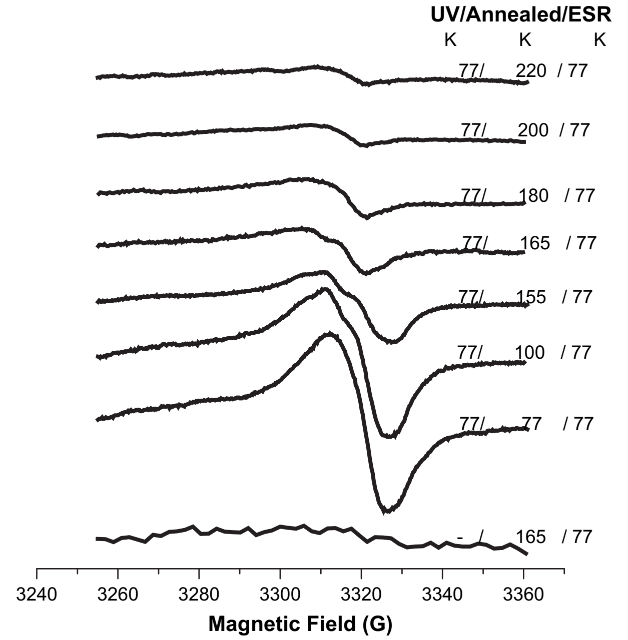

Fig. 1. Experimental (at 77 K) ESR spectra of UV-irradiated SPEEK membrane in acid form swollen by 3% H_2O_2/H_2O. The sample was annealed at indicated temperatures for 10 min. The spectra reveal the presence of •OH and •OOH radicals, as predominant radicals, until approximately 160 K. At about 160 K, the signal from the new species dominated the ESR spectrum.