Short communication

Direct ESR and spin trapping methods for the detection and identification of radical fragments in Nafion membranes and model compounds exposed to oxygen radicals

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Abstract

Direct electron spin resonance (ESR) and spin trapping methods are used in our laboratory in order to identify radical fragments in fluorinated membranes (Nafion) used in fuel cells and in model compounds when exposed to reactive oxygen species. Oxygen radicals were generated by the Fenton reaction, by the photo-Fenton method, and by UV-irradiation of aqueous H_2O_2 solutions. Direct ESR detection led to the identification of fluorinated radical fragments in UV-irradiated Nafion neutralized by Cu(II), Fe(II), and Fe(III) cations and exposed to H_2O_2. In Nafion exposed to the Fenton reagent in the presence of DMPO (5,5-dimethyl-1-pyrroline) as the spin trap, radical adducts of hydroxyl and carbon-centered radicals (CCRs) were detected. A fluorinated model compound, perfluro-(2-ethoxyethane) sulfonic acid ($CF_3CF_2OCF_2CF_2SO_3H$, PFEESA), that mimics the side chain of Nafion was chosen for study, with the goal to shed light on the more complicated degradation processes in the polymeric membranes. Analysis of the spin adducts obtained from UV-irradiated PFEESA in the presence of H_2O_2 and MNP (2-methyl-2-nitrosopropane) as the spin trap suggested that the side chain of Nafion is a possible site of attack by oxygen radicals.
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1. Introduction

Degradation of proton exchange membranes (PEMs) by reactive oxygen intermediates during fuel cell operation is a major problem that must be solved before the transition to a hydrogen economy. Direct electron spin resonance (ESR) is used by our group to detect and identify oxygen radicals [1] as well as radical intermediates formed in perfluorinated membranes [2] due to exposure to oxygen radicals in the laboratory; in these studies low temperatures is used to increase the lifetime of unstable intermediates, and gradual annealing at higher temperatures to follow the chemical transformations of each species.

For short-lived radicals at room temperature, spin trapping ESR methods were used to detect fragmentation of Nafion exposed to the Fenton reagent [3]. Spin trapping is based on scavenging of short-lived radicals, $^\bullet X$, by spin traps and formation of more stable adducts, typically a nitroxide radical [4–8]. DMPO (5,5-dimethyl-1-pyrroline), PBN (*N-tert*-butyl-α-phenylnitrone) and MNP (2-methyl-2-nitrosopropane), Chart 1a, are the most commonly used spin traps. The formation of the spin adduct for MNP as a spin trap is shown in Chart 1b.

In our recent work, spin trapping ESR was applied to model compounds for fluorinated PEMs, with the goal to assist in the interpretation of results and clarify the more complicated degradation processes in the polymeric membranes. Results obtained for perfluro-(2-ethoxyethane) sulfonic acid ($CF_3CF_2OCF_2CF_2SO_3H$, PFEESA) as the model compound are presented here [9]. Because of the presence of the ether linkage,

(a)

DMPO · PBN · MNP

(b) $(H_3C)_3C-NO + X^\bullet \longrightarrow (H_3C)_3C-N-X$
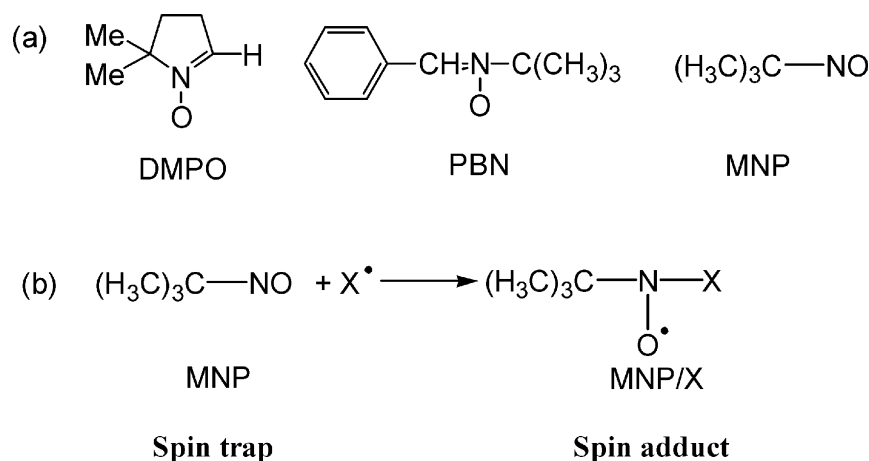MNP

MNP/X

Spin trap · **Spin adduct**

Chart 1. Common spin traps (a) and spin adduct formation for MNP (b).
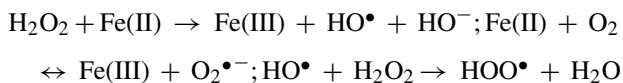
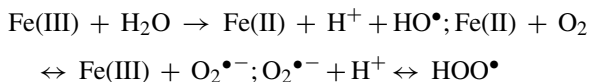PFEESA can be considered as a model compound for the Nafion side chain.

2. Experimental

2.1. Preparing oxygen radicals in the laboratory
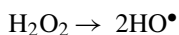
The three methods used are shown below.

(1) Fenton reaction [10]:

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + HO^\bullet + HO^-; Fe(II) + O_2$$
$$\leftrightarrow Fe(III) + O_2^{\bullet-}; HO^\bullet + H_2O_2 \rightarrow HOO^\bullet + H_2O$$

(2) Photo-Fenton reaction (UV-irradiation) [11]:

$$Fe(III) + H_2O \rightarrow Fe(II) + H^+ + HO^\bullet; Fe(II) + O_2$$
$$\leftrightarrow Fe(III) + O_2^{\bullet-}; O_2^{\bullet-} + H^+ \leftrightarrow HOO^\bullet$$

(3) Hydrogen peroxide decomposition by UV irradiation [12]:

$$H_2O_2 \rightarrow 2HO^\bullet$$

2.2. Sample preparation

In experiments with membranes exposed to the Fenton or photo-Fenton reagent based on Fe(II) and Fe(III), the membranes were partially neutralized with ferrous sulfate heptahydrate $FeSO_4 \cdot 7H_2O$, or ferric chloride hexahydrate $FeCl_3 \cdot 6H_2O$ solutions in water, dried in vacuum at ambient temperature, and exposed to 3% (w/v) aqueous solutions of H_2O_2. For spin trapping experiments, the aqueous solutions of H_2O_2 also contained DMPO (concentration 100 mM).

For the spin trapping experiments involving the model compound, samples were typically prepared by mixing 1 mL aqueous solutions of PFEESA from Matrix Scientific (concentration 0.1–2 mol L^{-1}), 0.1 mL aqueous solution of MNP from Sigma–Aldrich as spin trap (concentration 2×10^{-4} mol L^{-1}) and 0.05 mL of H_2O_2 (3% (w/v)) (Fisher). The pH of each solution was adjusted to pH ≈ 7 with 0.1 mol L^{-1} NaOH calibrated solution; this procedure was necessary because nitroxides

radicals are less stable in acid media [13]. Samples were UV irradiated *in situ* at 300 K in quartz capillary tubes placed inside the ESR resonator. A 300 W ozone free Xe arc (Oriel) equipped with a water filter was used as the UV source.

2.3. ESR measurements

X-band ESR spectra were recorded using Bruker X-band EMX spectrometers operating at 9.7 GHz with 100 kHz magnetic field modulation, equipped with the Acquisit 32 Bit WINEPR data system version 3.01 for acquisition and manipulation, and the ER 4111 VT variable temperature units. The magnetic parameters and relative intensities of spectral components were determined by computer simulation of experimental ESR spectra. Spectra in the rigid limit were simulated using SimFonia (Bruker) with manual parameter optimization. Solution spectra were simulated with the program WinSim (NIEHS/NIH); this software provided an automatic fit to the experimental spectra and also determined the relative intensity of each component in the case of a superposition of multiple components.

3. Results and discussion

3.1. Direct ESR radical detection in perfluorinated membranes

In UV-irradiated Nafion neutralized by Fe(II) (Nafion/Fe(II)) or by Fe(III) (Nafion/Fe(III)), weak ESR signals from perfluorinated radicals were detected at 77 K even in the absence of H_2O_2. The ESR signal increased significantly in intensity in the presence of H_2O_2, and was identified as the chain-end perfluorinated radical RCF$_2$CF$_2^\bullet$; this type of radical was previously detected in γ-irradiated Teflon [14,15]. The signal from Fe(III) was detected by ESR; the intensity of the RCF$_2$CF$_2^\bullet$ radical increased with irradiation time, while that of Fe(III) decreased. Experimental and simulated ESR spectra at 77 K for RCF$_2$CF$_2^\bullet$ in Nafion/Fe(II) and Nafion/Fe(III) at 77 K are seen in Fig. 1. The magnetic parameters used for the simulation confirmed the above identification of the ESR signal [2], which exhibits
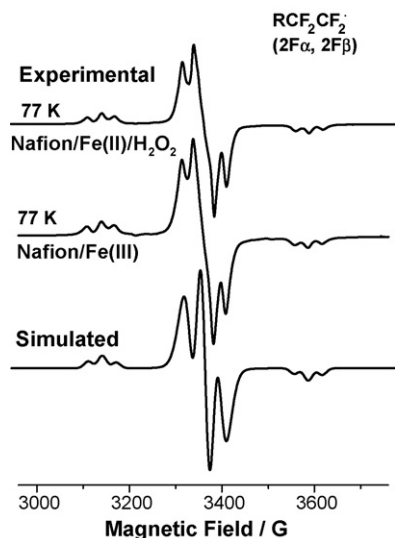
Fig. 1. ESR spectra at 77 K of the chain-end radical $RCF_2CF_2^\bullet$ in UV-irradiated Nafion/Fe(II)/H_2O_2/H_2O (degree of neutralization 40%) and in UV-irradiated Nafion/Fe(III) (degree of neutralization 10%), and the corresponding simulated spectrum.

Fig. 2. ESR spectra of DMPO adducts obtained in the system Nafion/Fe(II) (20%)/H_2O_2/DMPO/H_2O heated at 358 K for 3 h: temperature variation of ESR spectra. DMPO/OH and DMPO/CCR are the $^\bullet$OH and the carbon-centered radical adducts, respectively and are shown by arrows.

hyperfine splittings from four ^{19}F nuclei, two in α and two in β positions. It could be argued that this chain-end radical is formed by attack of HO$^\bullet$ on the end groups RCOOH of Nafion, which are known to be present as "impurities" vulnerable to attack by oxygen radicals [16,17]. However, the ^{19}F hyperfine splittings in the β position of the radical detected in Nafion are different compared to those detected in Teflon; for this reason we suggested that the chain-end radical detected in our experiments is formed by attack of oxygen radicals on the Nafion side chain.

Two additional radicals, with ESR spectra consisting of four lines with relative intensity approximately 1:3:3:1 ("quartet"), and five lines with relative intensities approximately 1:4:6:4:1 ("quintet") were detected when annealing the original sample above 200 K and were tentatively assigned to the two radicals shown in Chart 2 below.

3.2. Spin trapping by DMPO of radicals in nafion exposed to the Fenton reagent

The membranes exchanged with FeSO$_4$ (20%) were exposed to H_2O_2 at 358 K for 3 h ([H_2O_2]/[Fe(II)] = 550), followed by addition of the aqueous solution of DMPO as the spin trap. The temperature variation of the ESR spectra is shown in Fig. 2
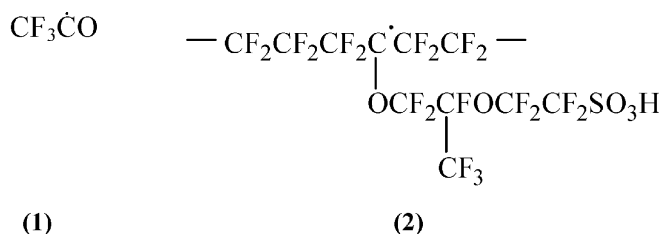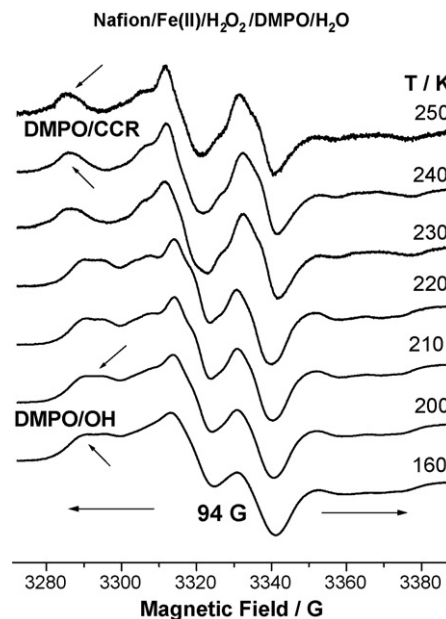
[3]. Below 230 K, the ESR spectra show the presence of the DMPO/OH adduct (near the rigid limit), while spectra at and above 230 K are typical of a carbon-centered radical adduct, DMPO/CCR. The only possible source of this adduct is Nafion, which is the only structure that can lead to carbon radicals. Therefore, the DMPO/CCR spin adduct was assigned to a Nafion-derived fragment; however, the chemical structure of the radical could not be identified. In accord with the spin trapping literature, these experiments indicated the preference of DMPO to trapping oxygen radicals and carbon-centered radicals (CCRs) [4–7].

3.3. MNP as a spin trap

Spin trapping experiments of radical fragments obtained by exposure of model compounds to HO$^\bullet$ radicals were initiated with the objective to shed light on the more complicated degradation processes in the ionomeric membranes. Because of the selectivity of spin traps for trapping of specific radicals, all three spin traps shown in Chart 1 were used in this study [18]. We present here the results obtained for PFEESA as the model compound and MNP as a spin trap.

$$CF_3\dot{C}O \qquad\qquad -CF_2CF_2CF_2\dot{C}CF_2CF_2-$$
$$\underset{\displaystyle\qquad\qquad\qquad CF_3}{\overset{\displaystyle OCF_2CFOCF_2CF_2SO_3H}{|}}$$

(1)   **(2)**

Chart 2. "Quartet" and "quintet" radicals in Nafion (via photo-Fenton treatment). (1) Quartet in Nafion, $a(3F_\beta) = 14.2$ G and (2) quintet in Nafion, $a(4F_\beta) = 22.5$ G.
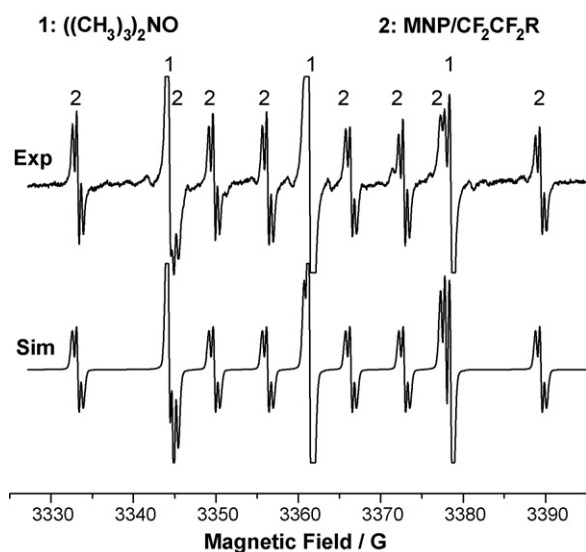
Fig. 3. Experimental and corresponding simulated ESR spectra of spin adducts detected at 300 K in PFEESA/MNP/H_2O_2 ([PFEESA] = 0.1 mol L^{-1}).

After 10 s of irradiation of an aqueous solution of H_2O_2 and MNP containing PFEESA (at low concentration, 0.1 mol L^{-1}), the ESR spectrum shown in Fig. 3 was measured, and interpreted in terms of a superposition of two signals: the triplet **1** with $a_N = 17.1$ G (from ^{14}N) was assigned to di-*tert*-butyl nitroxide (DTBN), derived from the spin trap; the triplet of triplets **2** where each signal has a 1:2:1 structure ($a_N = 16.6$ G; $a_\beta = 11.5$ G (2F) and $a_\gamma = 0.5$ G (2F)) was assigned to the MNP/CF_2CF_2R adduct [19–22].

For a higher PFEESA concentrations, 2 mol L^{-1}, two sets of lines appeared after irradiation, as shown in Fig. 4. Triplet **1** was assigned to DTBN, as in Fig. 3; the less intense triplet of doublets **3**, with $a_N = 16.6$ G; $a_\beta = 21.8$ G, was assigned to the MNP/F adduct.
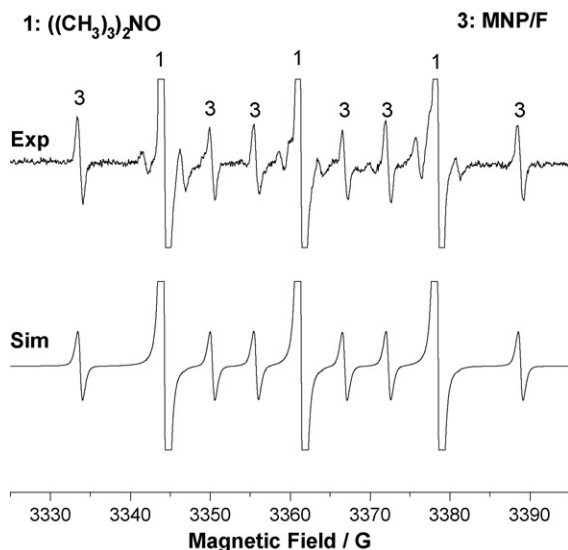

Fig. 4. Experimental and corresponding simulated ESR spectra of spin adducts detected at 300 K in PFEESA/MNP/H_2O_2 ([PFEESA] = 2 mol L^{-1}).

Two types of control experiments were performed in order to further validate the interpretation of the ESR spectra and the assignments of the spin adducts.

First, experiments were performed by irradiating the PFEESA and MNP solution in the absence of H_2O_2. The ESR spectrum reflected the presence of two spectral components: the triplet with $a_N = 17.1$ G, which was assigned to DTBN, spectrum **1** in Figs. 3 and 4, and a weak signal with $a_N = 14.6$ G, $a_H = 14.6$ G, which was assigned to the MNP/H adduct [20,23]. No other signals were detected.

Second, solutions of the model compound, MNP as the spin trap, and H_2O_2 dissolved in D_2O were irradiated, in order to verify that the splittings assigned to fluorine nuclei in adducts **2** and **3** are not due to protons. In these experiments, signals from the MNP/F and MNP/CF_2CF_2R adducts and from DTBN were detected. This result indicates that the splittings assigned to the ^{19}F nuclei in the fluorinated adducts are indeed from fluorine nuclei and not from other nuclei with $I = 1/2$, for example protons.

We note that the ^{19}F hyperfine splittings in the MNP/CF_2CF_2R adduct are lower than expected for fluorine nuclei in CF_2CF_2 groups directly connected to the spin trap, and more in line to a radical adduct of the type $RCF_2CF_2O^\bullet$. This radical may be a result of several reactions, possibly starting with the attack of HO$^\bullet$ radicals at α positions to the ether bond, and resulting in the cleavage of the side chain in PFEESA [24,25]. Such a mechanism is also expected to be valid in Nafion membranes [26]. Experiments are in progress in order to ascertain this suggestion.

4. Conclusions

The combination of direct ESR detection and spin trapping by two spin traps, DMPO and MNP, has provided complementary information on the identity of radicals in Nafion and in a model compound, $CF_3CF_2OCF_2CF_2SO_3H$ (PFEESA), exposed to oxygen radicals.

Attack of Nafion by oxygen radicals produced via the photo-Fenton method led to the identification of the $RCF_2CF_2^\bullet$ radical, based on hyperfine splittings from two α and two β ^{19}F nuclei. As the β splittings were different compared to those measured in γ-irradiated Teflon, we proposed that this radical is derived from the Nafion side chain.

Spin trapping by DMPO in Nafion exposed to the Fenton reagent at 358 K led to the detection of the DMPO/OH and DMPO/CCR adducts. The carbon-centered radical was not identified, but its source must be Nafion.

Spin trapping by MNP clearly demonstrated the formation of adducts of two perfluorinated adducts in CF_3CF_2-$OCF_2CF_2SO_3H$ (PFEESA) exposed to oxygen radicals produced by UV-irradiation of aqueous H_2O_2: MNP/CF_2CF_2R and MNP/F. As the structure of the model compound is similar to the side chain in Nafion, these results suggest that the side chain of Nafion can also be attacked by reactive oxygen species. Compared to DMPO, the MNP spin trap gives more direct information about the fluorinated radicals that are trapped.

Acknowledgements

References

[1] A. Bosnjakovic, S. Schlick, J. Phys. Chem. B 108 (2004) 4332–4337.
[2] M.K. Kadirov, A. Bosnjakovic, S. Schlick, J. Phys. Chem. B 109 (2005) 7664–7670.
[3] A. Bosnjakovic, S. Schlick, J. Phys. Chem. B 110 (2006) 10720–10728.
[4] E.G. Janzen, B.J. Blackburn, J. Am. Chem. Soc. 90 (1968) 5909–5910.
[5] E.G. Janzen, Acc. Chem. Res. 4 (1971) 31–40.
[6] C. Lagercrantz, J. Phys. Chem. 75 (1971) 3466–3475.
[7] G.M. Rosen, B.E. Britigan, H.J. Halpern, S. Pou, Free Radicals: Biology and Detection by Spin Trapping, Oxford University Press, New York, 1999.
[8] C. Motley, R.P. Mason, Biological Magnetic Resonance, vol. 8, Plenum, New York, 1989 (Chapter 10), pp. 489–546.
[9] S. Schlick, A. Bosnjakovic, M. Danilczuk, Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 51 (2) (2006) 688–689.
[10] C. Walling, Acc. Chem. Res. 8 (1975) 125–131.
[11] A.R. Freitas, G.J. Vidotti, A.F. Rubira, E.C. Muniz, Polym. Degrad. Stab. 87 (2005) 425–432.
[12] J. Bednarek, S. Schlick, J. Phys. Chem. 95 (1991) 9940–9944.
[13] B.J. Gaffney, in: L.J. Berliner (Ed.), Spin Labeling, Theory and Applications, Academic Press, New York, 1976, pp. 1830–2238 (Chapter 5).
[14] K. Toriyama, M. Iwasaki, J. Phys. Chem. 73 (1969) 2663–2670.
[15] K. Toriyama, M. Iwasaki, J. Chem. Phys. 73 (1969) 2919–2924.
[16] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, J. Power Sources 131 (2004) 41–48.
[17] J. Healy, C. Hayden, T. Xie, K. Olson, R. Waldo, A. Brundage, H. Gasteiger, J. Abbott, Fuel Cells 5 (2005) 302–308.
[18] M. Danilczuk, F. Coms, S. Schlick, in preparation.
[19] J.C. Evans, S.K. Jackson, C.C. Rowlands, M.D. Barratt, Tetrahedron 41 (1985) 5195–5200.
[20] J. Pfab, Tetrahedron Lett. 19 (1978) 843–846.
[21] K.P. Madden, H. Taniguchi, J. Am. Chem. Soc. 113 (1991) 5541–5547.
[22] Y. Katsumara, K. Ishigure, Y. Tabata, J. Phys. Chem. 83 (1979) 3152–3161.
[23] A.S.W. Li, C.F. Chignell, R.D. Hall, Photochem. Photobiol. 82 (1987) 379–382.
[24] http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/htmwg05_schiraldi.pdf (accessed 30 October 2006).
[25] D.A. Schiraldi, Polym. Rev. 46 (3) (2006) 215–217.
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