

Nafion Perfluorinated Membranes Treated in Fenton Media: Radical Species Detected by ESR Spectroscopy

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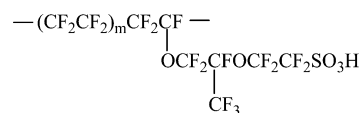
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ESR spectroscopy was used to detect and identify radicals in Nafion perfluorinated membranes exposed to the Fenton reagent based on Ti^{3+} ($\text{TiCl}_3 + \text{H}_2\text{O}_2$). This method allowed monitoring the disappearance of the ESR signal from Ti^{3+} during reaction. The initially formed radical was HOO^\bullet , with magnetic parameters $g_1 = 2.0261$, $g_2 = 2.0088$, $g_3 = 2.0031$ ($g_{\text{iso}} = 2.0127$), and $a_1 = 5$ G at 200 K. The disappearance of this radical above 220 K was accompanied by the appearance of a mixture of peroxy radicals TiOO^\bullet and superoxide radicals O_2^- . The O_2^- radicals were observed only in the dry Nafion after treatment and were stable up to 370 K; the g -tensor components are $g_1 = 2.0190$, $g_2 = 2.0092$, and $g_3 = 2.0036$ ($g_{\text{iso}} = 2.0106$) at 300 K. In samples swollen by the hydrogen peroxide solution, signals from the TiOO^\bullet radicals predominated, with g -tensor components $g_1 = 2.0228$, $g_2 = 2.0092$, and $g_3 = 2.0046$ ($g_{\text{iso}} = 2.0122$) at 200 K. A dynamical process lead to averaging of the g anisotropy of TiOO^\bullet radicals in the temperature range 220–320 K. The dynamics mechanism was identified with the “cubic jump” model: rotation of the O–O fragment about an axis equally inclined to the principal directions of the g tensor. A broad signal (line width ≈ 84 G, $g = 2.0023$) appeared in slightly dried samples after ≈ 14 days and increased in intensity after 92 days; this signal is thought to represent fluorinated alkyl radicals, formed by attack of oxygen radicals on the polymer chain. In the Fenton reagent (in the absence of Nafion) radicals are detected only for high concentrations of hydrogen peroxide, 30% w/v. In addition, the HOO^\bullet radicals formed are less stable, and the peroxy radicals TiOO^\bullet are the only species detected at and above 200 K. The presence of the Nafion membranes has important effects on both the type of radicals formed and their thermal stability.

Introduction

The science and technology relevant to chemical processes in fuel cells (FCs) have taken center stage in recent years because of the potential to provide a clean alternative to fossil fuels.¹ Current FC research led to progress in many areas, but problems remain and must be solved before the transition to a hydrogen, or/and methanol, economy.² A major component of a FC is the proton-exchange membrane (PEM), which is an *ionomer*: a polymer modified to include ions, typically sulfonic groups $-\text{SO}_3^-$. Ionomers self-assemble into hydrophobic and hydrophilic domains that, in a FC environment, allow the transport of H^+ in one direction only, from the anode to the cathode.³ The traffic light role fulfilled by the membrane was first demonstrated by Nafion, the ionomer made by DuPont, which consists of a perfluorinated backbone and pendant chains terminated by sulfonic groups (Scheme 1); this ionomer was the major component in the PEM-based FCs developed for the Gemini mission in the 1960s, to provide both energy and drinking water for space vehicles. The original FC was built around Pt as catalyst and Nafion as the PEM and operated at ≈ 80 °C. Important advantages in terms of water management in the cell and CO tolerance in the fuel can be gained by operating at higher temperatures, typically ≈ 120 °C;⁴ this operating temperature imposes additional stringent requirements in terms of membrane stability in a highly oxidative environment. Even at an operating temperature of 50 °C, evidence for the deterioration of Nafion membranes was detected by X-ray

SCHEME 1: Nafion Perfluorinated Polymer in Acid Form



powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS);⁵ moreover, it was reported that the type of structural damage is different at the anode and at the cathode sides.

The formation of reactive oxygen species during catalytic processes in FC operation has been amply demonstrated: H_2O_2 and HO^\bullet are the most commonly reported species,^{6,7} and their presence is implicated in membrane deterioration. The chemistries of H_2O_2 and of the HO^\bullet radical have been investigated for more than a century. In the laboratory, oxygen radicals can be produced by the Fenton reaction,⁸ where the major step is $\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{HO}^\bullet + \text{HO}^-$. Fenton reagents based on Ti^{3+} instead of Fe^{2+} have also been used.⁸ The formation of radical species from the attacked substrate, RH, is by H-abstraction $\text{HO}^\bullet + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^\bullet$; the R^\bullet radicals are derived from the polymer and can combine with triplet oxygen to produce peroxy radicals and thus initiate a degradation cascade. Currently the stability of FC membranes to oxidation is roughly assessed using the Fenton test: the polymer is soaked in an aqueous solution of H_2O_2 (3–30%) and FeSO_4 (4–30 ppm), and membrane stability is measured in terms of weight loss as a function of immersion time and time required for the membrane to break or to begin dissolving.^{9,10} This test provides

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no details on reactive intermediates, degradation mechanism, or factors that may affect the extent of structural damage.

Oxidation of sulfonated aromatics such as *p*-toluenesulfonic acid in UV-irradiated solutions of H_2O_2 in a flow system at ambient temperature has been used as a model for the degradation of sulfonated monomers relevant to FC applications; the degradation products have been identified by their ESR spectra and simulations, using known or reasonable magnetic parameters.¹¹ Reactions in self-assembled systems are, however, expected to be diffusion-controlled; for this reason, processes detected in homogeneous solutions may not be representative of realistic events expected in microphase-separated membranes.

The nature of unstable intermediates in Nafion and in self-assembled systems in general was also interrogated in our laboratory. The formation of the superoxide radical anion O_2^- was detected in dry Nafion neutralized by Ti^{3+} and exposed to oxygen and examined as a function of exposure time to oxygen.¹² The radicals are stable at and below 300 K and decrease in intensity above 310 K. Interestingly, the intensity of O_2^- radicals increased when the membrane was neutralized by a mixture of Al^{3+} and Ti^{3+} cations. This result is important because it implies that the amount of reactive intermediates is sensitive to the specific nature of counterions in the membranes.

The presence of oxidizing species such as HO^\bullet , HOO^\bullet , and O_2^- was detected by ESR in our study of UV-irradiated H_2O_2 solutions.¹³ The intensity of the corresponding ESR signals depended critically on the concentration of H_2O_2 . Radicals HO^\bullet and HOO^\bullet were identified by simulation of the ESR spectra based on magnetic parameters (*g*-values and hyperfine splittings from protons) and the assignments verified in experiments with D_2O as solvent, instead of H_2O .

We present a study of Nafion membranes exposed to the Fenton reagent based on Ti^{3+} ; this cation was chosen because of the ability to detect it by ESR and to monitor its disappearance during reaction.¹² As will be clearly demonstrated below, the results indicated that several types of oxygen radicals are formed, which lead to the formation of radicals derived from the membrane. The ESR spectra measured in the Nafion system were compared with results obtained in the Fenton reagent ($\text{TiCl}_3 + \text{H}_2\text{O}_2$), in the absence of the membrane.

Experimental Section

Materials. The Nafion 117 membranes, with an equivalent weight of 1100 g of polymer per mole of sulfonic groups and a thickness of 0.178 mm, were obtained from DuPont. In Scheme 1, $m = 6.5$; the mean repeat unit of the backbone consists therefore of 14 CF_2 groups and one CF group. Small pieces of membranes, $\approx 1 \times 2 \text{ cm}^2$, were stirred in isopropyl alcohol (reagent grade) for 2 h at ambient temperature, dry-blotted with filter paper, and dried in air at ambient temperature for 2 h. The membranes were then boiled slowly in 8 M HNO_3 under reflux for $\approx 1 \text{ h}$ and washed with deionized water; this step was repeated. After the second treatment with nitric acid, the membranes were boiled in deionized water for 0.5 h. The treated membranes were stored in deionized water. For ESR measurements, the membranes were vacuum-dried (10^{-4} Torr) for 24 h at ambient temperature and for 1 h at 373 K.

TiCl_3 , supplied by Aldrich and shipped in a pouch under nitrogen, was opened and stored in a glovebox under nitrogen. Aqueous solutions of H_2O_2 (30% and 3% w/v) were from Fisher Scientific. Methanol was dehydrated using molecular sieves Type 3A (Fisher) and deaerated in the glovebox by a stream of nitrogen.

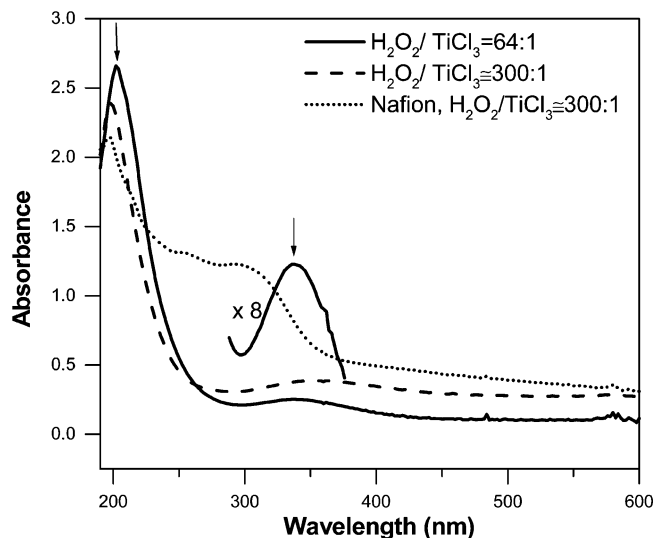


Figure 1. UV spectra at ambient temperature for the indicated concentrations of the Fenton reagent (full and dashed lines) and for Nafion/ $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ (dotted line).

Sample Preparation. Nafion membranes were fully neutralized with $8.64 \times 10^{-3} \text{ M}$ TiCl_3 solution in methanol, equilibrated for 24 h, rinsed in methanol, dry-blotted with filter paper, and transferred to 4 mm o.d. quartz ESR sample tubes; all these steps were carried out in the glovebox under nitrogen gas. We found that Ti^{3+} is more stable in methanol compared to water.¹² The membrane pieces were vacuum-dried (10^{-4} Torr) for 24 h at room temperature and 1 h at 373 K and exposed in the glovebox to the aqueous H_2O_2 solution. Spectra of the Fenton solution ($\text{TiCl}_3 + \text{aqueous } \text{H}_2\text{O}_2$ solution) were measured in capillary tubes prepared by flame-sealing of disposable pipets.

ESR Measurements. Spectra were recorded with Bruker X-band EMX spectrometers operating at 9.7 GHz with 100 kHz magnetic field modulation and 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 microwave frequency was measured with a Hewlett-Packard 5350B microwave frequency counter. Most spectra were collected with the following parameters: sweep width 600 G, microwave power 2 mW, time constant 40.96 ms, conversion time 81.92 ms, 4–10 scans, and 1024–2048 points. The modulation amplitude was 3.2 G in most cases. The temperature was controlled within $\pm 1 \text{ K}$. All samples were allowed to equilibrate for at least 10 min after reaching the desired temperature. Additional experimental details have been described.^{14,15}

Results and Discussion

In this section we will provide evidence for the formation of HOO^\bullet , O_2^- , TiOO^\bullet , and fluorinated alkyl radicals in Nafion/ $\text{Ti}^{3+}/\text{H}_2\text{O}_2$. Separate signals from these radicals species were obtained by variation of sample preparation methods, temperature used for spectra acquisition, and annealing conditions. The formation and stability of these radicals will be compared to those of radicals present in the Fenton reagent ($\text{TiCl}_3 + \text{H}_2\text{O}_2$).

Upon addition of the H_2O_2 solution, the neutralized membranes became yellow-red, indicating the presence of diamagnetic Ti^{4+} complexes.^{16,17} The color was detected also in the Fenton reagent (no Nafion) and appeared even when the H_2O_2 concentration was 3%. As seen in Figure 1, the UV spectra from the Fenton reagent consist of two major signals at $200 \pm 2 \text{ nm}$ and in the range 338–354 nm. These signals are similar to those

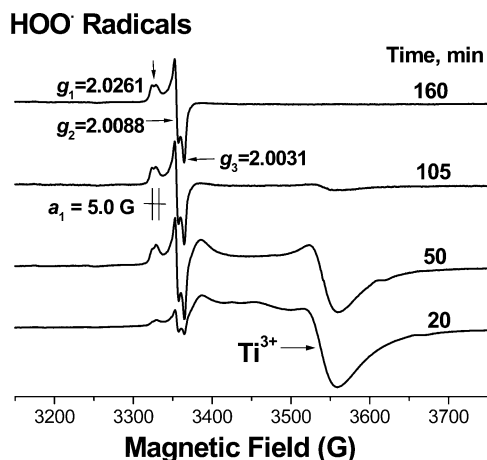
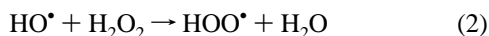
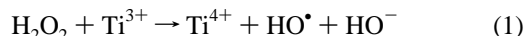


Figure 2. X-band ESR spectra at 200 K of dry Nafion fully equilibrated by Ti^{3+} and exposed to the H_2O_2 solution (30% w/v) as a function of contact time. The g -tensor components and the proton hyperfine splitting for HOO^\bullet are indicated.

assigned recently to ligand-to-metal charge transfer (LMCT) in diamagnetic dimeric peroxo Ti^{4+} complexes¹⁸ and have the same metal ion electronic configuration as the yellow-red complexes of V^{5+} catalysts reacted with excess of H_2O_2 solutions.¹⁹ In the Nafion system, a band at 198 nm and a broad band in the vicinity of 290 nm were detected (Figure 1) and are likely to represent similar Ti^{4+} species. No ESR signals are expected from these complexes.

HOO• Radical. X-band ESR spectra at 200 K of Nafion membranes fully neutralized by Ti^{3+} and in contact with an aqueous solution containing 30% H_2O_2 are shown in Figure 2 as a function of contact time. The molar ratio $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ was $\approx 1:300$. The broad high-field signal is attributed to Ti^{3+} ,¹² whose spectrum is prominent for exposure times of 20 and 50 min. The weak anisotropic signal near $g \approx 2$ seen after exposure time of 20 min increased in intensity with contact time and dominates the spectrum after 100 min of contact. This signal, with $g_1 = 2.0261$, $g_2 = 2.0088$, $g_3 = 2.0031$ ($g_{\text{iso}} = 2.0127$), and $a_1 = 5$ G, is attributed to HOO^\bullet radicals; g_1 is in the direction of the O–O bond, g_2 is in the molecular plane, and g_3 is perpendicular to the molecular plane.²⁰ This assignment is logical, as HOO^\bullet radicals are produced in a Fenton reagent from HO^\bullet radicals in the presence of excess H_2O_2 :⁸



The line shape of HOO^\bullet (Figure 2) is similar to that assigned to HOO^\bullet radicals detected at 77 K in UV-irradiated aqueous H_2O_2 solutions and $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ solutions adsorbed on silica gel,¹³ with $g_{\text{iso}} = 2.0138$ and $a_1 = 12.3$ G. Slightly different values were reported in another study of $\text{H}_2\text{O}/\text{H}_2\text{O}_2$ solutions that were irradiated with UV or ionizing radiation:²⁰ $g_{\text{iso}} = 2.0160$ and $a_1 = 14$ G. These values are higher than those in the Nafion system but in line with the extreme sensitivity of the magnetic parameters for HOO^\bullet radicals to the local environment.^{13,21,22} We note that the g values deduced from Figure 2 are in the range reported for signals attributed to either HOO^\bullet or HO^\bullet radicals ($g = 2.0117$ and 2.0102) in Fenton reactions and fast-flow techniques.^{16,17} Usually HO^\bullet radicals are detected only at low temperatures (≤ 77 K)¹³ or by spin trapping.^{19,23,24}

HOO^\bullet radicals were also obtained in Nafion/ Ti^{3+} for H_2O_2 concentrations of 20 and 3%. The intensities of these signals

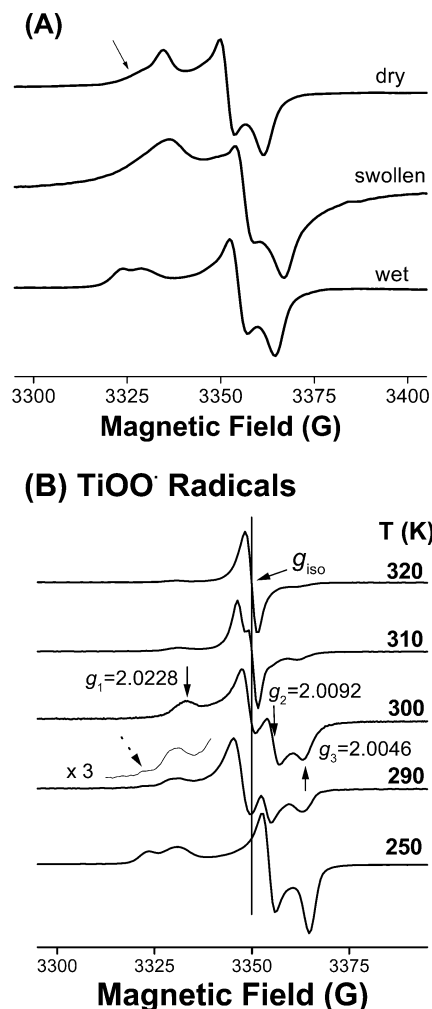
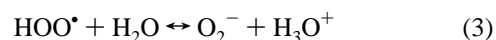


Figure 3. X-band ESR spectra at 200 K of dry Nafion fully equilibrated by Ti^{3+} and exposed to the H_2O_2 solution (30% w/v): (A) as the sample is dehydrated; (B) in the swollen sample, as a function of temperature. The g -tensor components for TiOO^\bullet are indicated; the vertical line is drawn at a magnetic field corresponding to g_{iso} . See text.

were slightly lower and a_1 slightly higher: a_1 was 6 G for the Nafion system containing 20% H_2O_2 (molar ratio of $\text{Ti}^{3+}/\text{H}_2\text{O}_2 \approx 1:200$) and 7 G for the system 3% H_2O_2 (molar ratio of $\text{Ti}^{3+}/\text{H}_2\text{O}_2 \approx 1:25$).

Peroxy Radical TiOO^\bullet . X-band ESR spectra at 200 K, measured upon progressive removal of the H_2O_2 solution from the membrane, are shown in Figure 3A. The lower spectrum is the “signature” line shape of the HOO^\bullet radical. This signal disappears on drying, most likely because the presence of HOO^\bullet radicals depends on the presence of H_2O_2 , as clearly described in reactions 1 and 2. The major signal in the dry sample (top spectrum in Figure 3A) has the g -tensor components typical for O_2^- radicals ($g_1 = 2.0190$, $g_2 = 2.0092$, $g_3 = 2.0036$, ± 0.0005 ($g_{\text{iso}} = 2.0106$)).¹² The shoulder indicated by the arrow in the top spectrum, however, indicates the presence of an additional species. The middle spectrum in Figure 3A is clearly a superposition of two signals, with similar g_2 and g_3 values. At this point we tentatively assign the composite spectra to contributions from O_2^- and peroxy radicals TiOO^\bullet . The formation of these species is described in reactions 3 and 4:



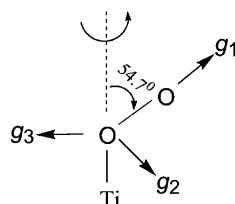


Figure 4. “Cubic jump” rotation model for the peroxy radical TiOO^\bullet . The rotation axis is assumed to be along the $\text{Ti}-\text{O}$ bond, and the angle between this axis and the $\text{O}-\text{O}$ bond is 54.7° .

TABLE 1: Magnetic Parameters of the Radicals in Nafion/ $\text{Ti}^{3+}/\text{H}_2\text{O}_2$ ^a

species	g_1	g_2	g_3	g_{iso}	a_1 (G)
HOO^\bullet	2.0261	2.0088	2.0031	2.0127	5.0
TiOO^\bullet	2.0228	2.0092	2.0046	2.0122	
O_2^-	2.0190	2.0092	2.0036	2.0106	
R^\bullet (from Nafion)				2.0023	

^a The \mathbf{g} -tensor components were measured ± 0.0005 . Parameters for HOO^\bullet , TiOO^\bullet , and O_2^- were measured at 200 K and for R^\bullet at 300 K.

According to reaction 3, HOO^\bullet is expected to be more stable in acidic media.^{16,17} Indeed, we found this to be true in Nafion samples that were less than fully neutralized by Ti^{3+} , for example 80%; the membrane acidity is higher at low degrees of neutralization.

Support for the formation of the peroxy radical TiOO^\bullet is obtained from the spectra presented in Figure 3B for fully neutralized Nafion swollen by $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (30% w/v H_2O_2) and measured in the temperature range 250–320 K. The spectrum at 250 K is similar to that detected for HOO^\bullet (Figure 2), but the lines are broader. Moreover, the low-field doublet is not symmetrical and is replaced in the spectrum measured at 290 K by one line; the dotted arrow in Figure 3B points to the low-field signal from HOO^\bullet , suggesting a mixture of radicals. The spectrum measured at 300 K has clear signals corresponding to $g_1 = 2.0228$, $g_2 = 2.0092$, and $g_3 = 2.0046$ ($g_{\text{iso}} = 2.0122$). The additional signal at $g_{\text{iso}} \approx 2.0122$ is evidence for a dynamical effect. As the temperature increased, the signals corresponding to the rhombic \mathbf{g} tensor became weaker and the isotropic signal stronger. At 320 K the isotropic signal dominates. The principal values of the \mathbf{g} tensor are in the range of values determined for peroxy radicals in various systems.^{25,26} The dynamic effect was demonstrated by the reproducibility of the spectra as the temperature is cycled in the range 290–320 K.

The variation of the line shapes with temperature is identical to that predicted by the “cubic jump” mechanism described in our studies of dynamics in peroxy radicals: interconversion between three sites by rotation about an axis that is equally inclined (at the magic angle of 54.7°) to the principal axes of the \mathbf{g} tensor.^{25,26} The model corresponds to rotation around the body diagonal of a cube. Calculated spectra as a function of the mean lifetime, τ , of all sites (Figure 7 in ref 26) reproduce accurately the temperature variation of the spectra given in Figure 3B. If we assume that the dynamics is the rotation around the $\text{Ti}-\text{O}$ bond, as shown in Figure 4, we deduce that the $\text{Ti}-\text{O}-\text{O}$ angle is equal to the magic angle, 54.7° . It is interesting to note that the directions of the g_2 and g_3 are not in the TiOO^\bullet plane or perpendicular to it. The corresponding \mathbf{g} -tensor components are given in Table 1.

Superoxide Radical O_2^- . In Figure 5 we present ESR spectra in dry Nafion membranes fully equilibrated with Ti^{3+} and exposed to H_2O_2 solutions (30% w/v), as a function of temperature. The signal is assigned to O_2^- , with $g_1 = 2.0190$,

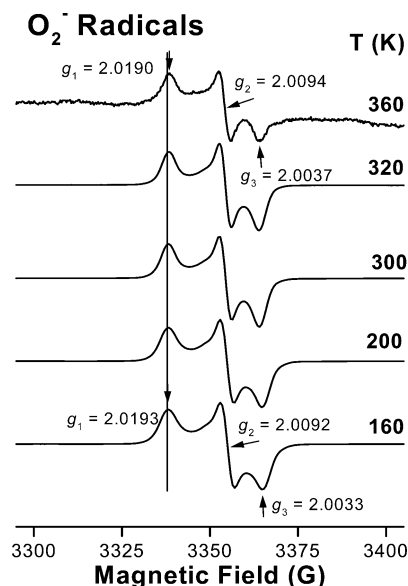


Figure 5. X-band ESR spectra of O_2^- in the dry sample as a function of temperature. The \mathbf{g} -tensor components at 160 and 360 K are indicated.

$g_2 = 2.0092$, and $g_3 = 2.0036$ ($g_{\text{iso}} = 2.0106$) at 300 K. These g values are in accord not only with our previous study¹² but also with values determined in titania gels²⁷ and during the photocatalytic epoxidation by molecular oxygen of propene on $\text{TiO}_2-\text{SiO}_2$ binary oxides.²⁸ The g_1 value, along the $\text{O}-\text{O}$ bond, is very sensitive to the local electric field from the surrounding electric charges and is used to identify the local environment of the radical in different media.^{12,16,26,29} As seen in Figure 5, the \mathbf{g} -tensor components are stable in the temperature range 160–360 K, but the signal intensity decreased on heating above 360 K. In samples kept at room temperature, the signal disappeared after ≈ 14 days.

The results presented in Figures 3 and 5 indicate that two radicals, TiOO^\bullet and O_2^- , are formed from the initial HOO^\bullet radicals in Nafion treated in Fenton media. TiOO^\bullet was detected in swollen Nafion and was characterized by the principal values of the \mathbf{g} tensor and by the dynamical process that lead to averaging of the tensor components; O_2^- radicals were detected only in dry Nafion. It is important to note that in samples that are not completely dry a weak shoulder corresponding to the g_{iso} for TiOO^\bullet was observed, as clearly indicated by the arrow in Figure 3A.

Fluorinated Alkyl Radicals. In Figure 6 we present the evolution of X-band ESR spectra at 300 K in Nafion/ Ti^{3+} that was treated with the H_2O_2 solutions, as a function of storage time at ambient temperature. The bottom spectrum in Figure 6 is a mixture of TiOO^\bullet (the low field signal is indicated by the arrow) and O_2^- radicals. After 14 days, the central signal is weaker and is accompanied by a broad signal with $g \approx 2.0023$. This signal is stronger after 92 days (top spectrum in Figure 6); the arrows in Figure 6 are separated by ≈ 84 G. We assign this signal to fluorinated alkyl radicals. Hyperfine splittings from fluorinated radicals have been widely investigated in single crystals and disordered media. In small fluorinated molecules typical values for $a_{\text{iso}}(\text{F})$ are large, in the range 60–150 G for α -fluorine and 20–70 G for β -fluorine.³⁰ Fluorine hyperfine splittings in the chain radical and in the end radical in γ -irradiated poly(tetrafluoroethylene) (PTFE) have also been deduced: 90 G for α -fluorine and 33 G for β -fluorine in the chain radical and corresponding values of 170 and 16 G in the end radical.^{31,32} At this stage we cannot identify the exact nature

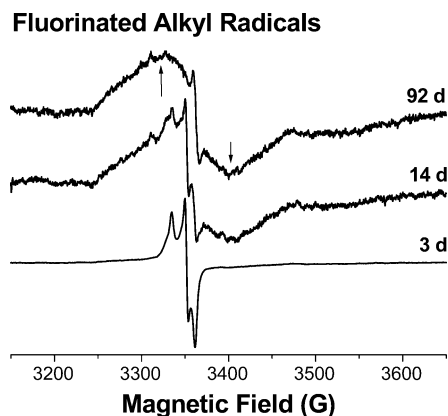


Figure 6. X-band ESR spectra at 300 K of the swollen Nafion sample that was treated with the solution (30% w/v), as a function of time. Arrows indicate the approximate line width of the broad signal (84 G), which was assigned to fluorinated alkyl radicals.

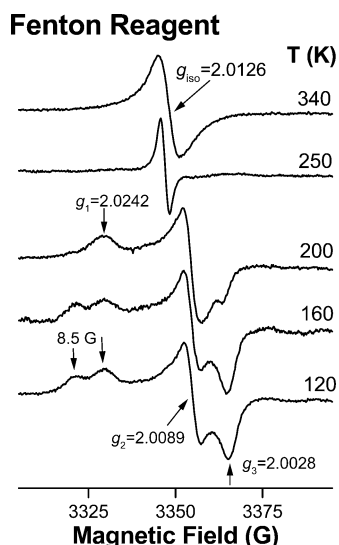


Figure 7. X-band ESR spectra of the Fenton reagent based on Ti^{3+} , as a function of temperature. The molar ratio $\text{H}_2\text{O}_2/\text{TiCl}_3$ was 64:1.

of the fluorinated alkyl radicals responsible for the broad signal, but its width and g value are in the range expected for fluorinated radicals. Work along these lines continues in our laboratory.

The fluorinated radicals were formed after the O_2^- radicals were expected to disappear; for this reason we suggest that the Nafion chains were attacked by the peroxide radicals, TiOO^\bullet .

Radicals in the Fenton Reagent. ESR spectra obtained in $\text{TiCl}_3/\text{H}_2\text{O}_2$ (30% w/v) are shown in Figure 7, as a function of temperature in the range 120–340 K. The molar ratio of $\text{H}_2\text{O}_2/\text{TiCl}_3$ was 64:1. Two radicals were identified: HOO^\bullet and TiOO^\bullet . The stability of HOO^\bullet radicals is lower than in the Nafion system: even at 120 K (Figure 7) the two low-field signals are not symmetrical and indicate a mixture of the two radicals. At 200 K only TiOO^\bullet was detected, and the isotropic signal due to dynamical averaging was seen at 250 K. Broadening of the signal at 340 K is assigned to spin-rotation interaction.³³ The same spectra were obtained when the molar ratio $\text{H}_2\text{O}_2/\text{TiCl}_3$ was increased to 300:1 to mimic the conditions in the Nafion system. No signals were detected when the concentration of H_2O_2 was lower, 20 or 3% w/v.

Comparison of spectra presented in Figures 3B and 7 emphasizes the effect of the environment on the stability of radical species obtained in the Fenton reaction. The main effects of the Nafion matrix are increased stability of HOO^\bullet radicals, decreased rate of dynamical averaging for the TiOO^\bullet radicals,

and formation of O_2^- radicals. Radical stabilization by the matrix is also seen in the higher concentration of H_2O_2 needed to form the radical species in the Fenton reagent.

Comparison of Nafion/ $\text{Ti}^{3+}/\text{O}_2$ with Nafion/ $\text{Ti}^{3+}/\text{H}_2\text{O}_2$. The only radical detected in Nafion neutralized by Ti^{3+} and exposed to oxygen was O_2^- . By contrast, in the Fenton medium we detected the initial formation of HOO^\bullet species, which was transformed at temperatures above 200 K into a mixture of TiOO^\bullet and O_2^- radicals. It was possible to determine these two radicals separately by variation of the degree of swell in the polymer: The peroxy-type radical was detected in moderately wet membrane, and its dynamics was identified. O_2^- radicals were detected only in dry samples.

Conclusions

ESR spectroscopy was used to detect and identify radicals in Nafion perfluorinated membranes exposed to the Fenton reagent based on Ti^{3+} . The disappearance of the ESR signal from paramagnetic Ti^{3+} and the appearance of oxygen radicals were monitored as a function of reaction time. The disappearance of the signal from Ti^{3+} was accompanied by the appearance of HOO^\bullet radicals, with the following magnetic parameters: $g_1 = 2.0261$, $g_2 = 2.0088$, $g_3 = 2.0031$ ($g_{\text{iso}} = 2.0127$), and $a_1 = 5$ G. These initially formed HOO^\bullet radicals disappeared above 220 K, and a mixture of peroxy radicals TiOO^\bullet and superoxide radicals O_2^- was detected. The O_2^- radicals were observed only in dry Nafion, were stable for ≈ 14 days at ambient temperature, and disappeared on heating to 370 K. The corresponding g -tensor components are $g_1 = 2.0190$, $g_2 = 2.0092$, and $g_3 = 2.0036$ ($g_{\text{iso}} = 2.0106$). In wet samples signals from the TiOO^\bullet radicals predominate, with g -tensor components of $g_1 = 2.0228$, $g_2 = 2.0092$, and $g_3 = 2.0046$ ($g_{\text{iso}} = 2.0122$). A dynamical process lead to averaging of the g anisotropy of TiOO^\bullet radicals in the temperature range 220–320 K. The dynamical mechanism was identified with the “cubic jump” model: rotation about an axis equally inclined to the principal directions of the g tensor. A broad signal (line width ≈ 84 G, $g = 2.0023$) appeared in dry samples after ≈ 14 days and increased in intensity after 92 days; this signal is thought to represent fluorinated alkyl radicals, formed by attack of the TiOO^\bullet radicals on the polymer.

In the Fenton reagent (TiCl_3 + hydrogen peroxide, no Nafion) radicals were detected only for high concentrations of hydrogen peroxide, 30% w/v. In addition, the HOO^\bullet radicals were less stable, and the peroxy radicals TiOO^\bullet were the only species detected at and above 200 K.

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