

Mechanism of Oxygen Response in Carbon-Based Sensors

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The mechanism of oxygen response in several newly synthesized oxygen-sensitive chars was studied with the use of EPR spectroscopy. The results suggest that the compounds contain two basic types of paramagnetic centers (PC). The change in oxygen concentration leads to a mutual and reversible transformation of PCs in chars, which is reflected in EPR parameters. The adsorbed molecular oxygen progressively disturbs the wave functions of the PCs and so breaks the Heisenberg exchange between them. At high oxygen concentration, the 2D dipole–dipole interaction between PCs at the surface comes into play and determines the EPR lineshape. A suggested model quantitatively describes the evolution of the basic EPR parameters of each PC as a function of oxygen concentration.

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I. INTRODUCTION

The development of more sensitive, highly localized, noninvasive *in vivo* measurement techniques for molecular oxygen concentrations is important because of the central role that O₂ plays in a variety of normal and pathological processes in cells and tissues (1, 2). The effect of molecular oxygen on the EPR linewidth of paramagnetic centers (PC) present in carbon chars was revealed in the 1960s (3, 4). This effect, by which molecular oxygen broadens the EPR line in a reversible and reproducible manner, has become the basis for EPR oximetry.

A low-temperature pyrolysis process was recently developed at the Illinois EPR Research Center for the production of a class of carbon-based chars for use in EPR magnetic resonance oximetry (5, 6). The carbons are chemically stable and biologically inert, and have reduced detection limits for molecular oxygen by several orders of magnitude over the most sensitive existing methods.

Despite intensive EPR investigations in such systems, the origin of the PC and the mechanism of their oxygen response are not yet clear. The objective of this paper is to suggest a new possible mechanism of oxygen response in newly synthesized chars.

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II. EXPERIMENTAL

Samples of chars were produced by a highly controlled low-temperature pyrolysis of carbonaceous materials, obtained from various kinds of woods, by charring under H₂ flow. The samples were heated at an increasing rate of 10°C per hour with a maximum temperature ranging from 420 to 720°C. Preparation techniques included digitally programmed temperature profiles, ball milling, and size separation by microsieving. Details of char synthesis are described elsewhere (5, 6). The most accurate measurements were performed on Peltogyne, the exotic South American hardwood, and fructose chars. Other hardwoods and softwoods listed in Refs. (5, 6), such as Red Cedar and starch, were also studied.

EPR measurements were performed on a Bruker EPR X-band spectrometer (ER-200, 9.7 GHz) at room temperature (295 K). The samples of dry chars were placed in a quartz tube and evacuated to a pressure of 2×10^{-2} Torr.² Spectra then were taken at pressures between the lowest value and atmosphere. Such a procedure enabled us to study the evolution of the EPR spectrum in an O₂ concentration range covering five orders of magnitude. The absolute concentrations of the PCs were determined from the area under the EPR absorption line by double integration of the derivative signal. A reference sample (MgO:Mn) was used for calibration.

III. RESULTS

At atmospheric pressure, all the studied chars demonstrate similar EPR lineshape, consisting of a narrow central part (the peak-to-peak linewidth $\delta H_{pp} \sim 10$ G) and wide wings extended out to hundreds of gauss. After evacuation, the δH_{pp} value decreases down to a few tenths of gauss, whereas the amplitude of the EPR signal increases several orders of magnitude, due to contraction of the broad wings (Fig. 1). These transformations of the EPR spectra were found to be reversible with changes of oxygen concentration. The characteristic time of approaching the steady state was less than 1 s. The whole PC concentration,

² Throughout this paper we will use Mol/l units for oxygen concentration, taking into account that the atmospheric air pressure of 760 Torr corresponds to oxygen concentration $c = 9.38 \times 10^{-3}$ Mol/l.

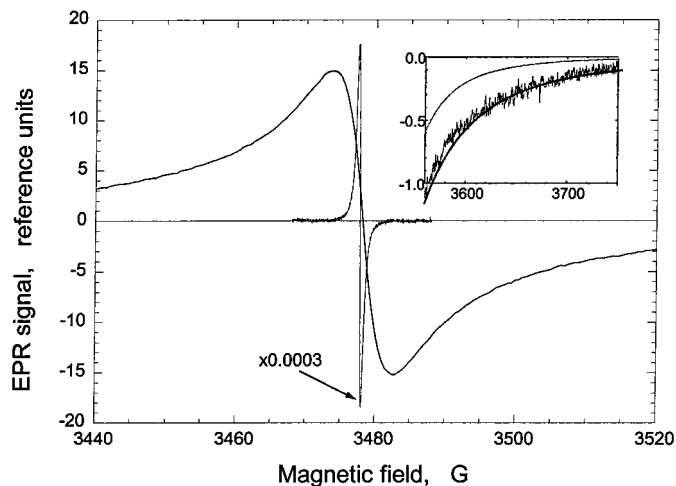


FIG. 1. EPR spectra of “Peltogyne” char at 2×10^{-2} Torr (narrow line) and 760 Torr (broad line). Note the scale change for the magnitude of the narrow line. Inset: the distant wing of the spectrum at 760 Torr and the best fit using Lorentzian (dashed curve) and 2D dipolar (solid curve) approximations (see the text).

as determined from the area of the EPR absorption, was found to be constant within the whole range of oxygen content variation. In particular, a PC concentration of $4.7 \times 10^{19} \text{ g}^{-1}$ was measured in chars produced from Peltogyne. Qualitatively, the evolution of the EPR spectrum caused by oxygen was similar for all newly synthesized chars described in Refs. (5, 6), and the “Peltogyne” sample was selected in this work in order to illustrate general trends of char oxygen behavior.

Figure 1 demonstrates typical evolution of the EPR spectrum of chars with changes of oxygen concentration. A simple analysis shows that generally the EPR lineshape cannot be approximated by either a single Lorentzian or Gaussian curve. In accordance with Ref. (6) two superimposed Lorentzian lines are needed to fit the spectra at low concentration of oxygen. Each of the lines corresponds to a different kind of PC in chars: centers *A* form the broader EPR component, while centers *B* form the narrower one. The fitting procedure results in a good approximation of the lineshape (the residual is at the level of noise in the experiment) within the O_2 concentration changed from 5×10^{-7} to $3 \times 10^{-3} \text{ Mol/l}$, and a simple two-site exchange model between sites *A* and *B* accounts well for changes in δH_{pp} with O_2 in two regions (6).

At O_2 concentrations higher than $3 \times 10^{-3} \text{ Mol/l}$, the EPR lineshape changes, and a simple superposition of two Lorentzian lines no longer can be used to approximate the spectrum. The inset in Fig. 1 shows that at the oxygen concentration the line wings fall off much slower than those for a two-Lorentzian superposition. Thus not only does broadening of the EPR line occur, but also a substantial change in the lineshape at oxygen concentrations above $3 \times 10^{-3} \text{ Mol/l}$. We suggest that this transformation is due to the crossover from the regime of exchange narrowing to dipolar broadening of the EPR line. A theoretical basis is presented in Section IV.

Let us consider the oxygen behavior of EPR parameters in more detail. Figure 2 shows the basic parameters fitted for each component contributing to the experimental EPR line: (a) integrated intensities, which are proportional to the concentration of the corresponding PC, and (b) transverse relaxation time T_2 , which is characteristic of the corresponding linewidth (the theoretical expressions for T_2 are given in the next section). One can see from Fig. 2a that the increase of oxygen concentration results in a monotonic decrease of the concentration of centers type *B*, which form the narrower EPR line component. At the same time, the concentration of type *A* centers monotonically increases. This behavior suggests that *initially* the centers *B* have no oxygen in their nearest neighborhood, while the centers *A* have. As the concentration increases, oxygen molecules enter sites near the paramagnetic centers *B*, thus transforming them to centers *A*. As a result the fraction of radicals having neighboring oxygen (centers of type *A*) increases progressively, while the concentration of centers *B* decreases. It should be emphasized that over the whole range of the oxygen concentration the total amount of the radicals ($A + B$) remains constant. This fact supports a model in which there is a *mutual transformation* of different types of paramagnetic species. Note that the oxygen behavior of EPR parameters is reversible with a short characteristic time not exceeding 1 s, thus suggesting a physical nature of char–oxygen interactions.

The char samples studied in the present work are porous materials. One can suggest that the *A* centers are situated in the pores containing adsorbed oxygen, whereas the *B* centers occupy the oxygen-free pores. So the influence of the oxygen molecules

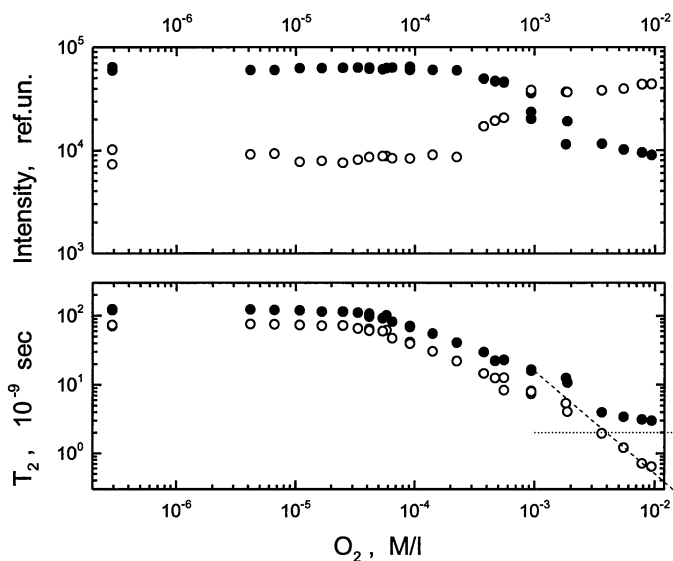


FIG. 2. The dependencies of the fitting parameters of the EPR spectrum in “Peltogyne” char on the oxygen concentration in ambient air. Open and solid symbols correspond to *A* and *B* components of the spectrum, respectively. Dashed and dotted lines represent the asymptotic behavior of T_2 at high oxygen concentration (see the text).

on the A spin system is more pronounced than on the B one, the latter being separated from the oxygen molecules by pore walls (at least tens of ångströms). As the oxygen concentration increases, some more accessible pores can be filled first (7). As a result, T_2 starts to decrease for both kinds of centers, whereas the A and B populations begin to change only at higher c values, when oxygen enters other pores, see Figs. 2a, 2b.

IV. DISCUSSION

Low oxygen concentration ($c < 3 \times 10^{-3}$ Mol/l). If we assume a homogeneous distribution of PC in chars, one can easily estimate that with the given PC concentration ($\approx 5 \times 10^{19}$ g $^{-1}$) the magnetic dipole–dipole (d–d) broadening of the EPR line must be about 10 G. Consequently the EPR linewidth of a few tenths of gauss, which is experimentally observed at low oxygen pressures, is due to electron–electron Heisenberg exchange narrowing. The purely Lorentzian lineshape typical of the exchange-narrowed EPR spectra (8) is observed (Fig. 1). The existence of antiferromagnetic exchange in similar systems has already been demonstrated experimentally (9). It was also suggested that the exchange process between paramagnetic species can be affected by molecular oxygen (superexchange) even at small oxygen concentrations. However, if superexchange through labile oxygen were important, evacuation of the sample should lead to EPR broadening due to the removal of oxygen needed for the superexchange. This was not observed experimentally (see Fig. 2), suggesting that Heisenberg exchange occurs directly between PCs, without oxygen molecules as intermediaries.

At low oxygen concentrations the EPR linewidth, strongly narrowed by the exchange interaction can be estimated by the formula (8)

$$\delta_{ex} \approx \frac{M_2}{J}, \quad [1]$$

where M_2 is the second moment of the line caused by d–d interaction and J is the exchange integral. Equation [1] is valid only if the exchange integral J is much larger than the d–d interactions between PCs:

$$J \gg M_2^{1/2}. \quad [2a]$$

In magnetically diluted solids, M_2 is related to the dipolar half-width of the EPR line (8),

$$M_2 \approx \alpha \delta_d, \quad [2b]$$

where α is an energy determined by the d–d interaction between nearest PCs. Since δ_d characterizes the d–d interactions at a mean distance, then obviously $\alpha \gg \delta_d$. Hence in a diluted system, $M_2^{1/2} \gg \delta_d$ (see, for example, Ref. (8)). Combining Eqs. [2a] and [2b] one can conclude that at the lowest O₂ concentration, the J

value exceeds the dipolar linewidth by two orders of magnitude and can reach 10³ G, a figure which is in good agreement with J evaluated from static susceptibility measurements (9).

Relatively high oxygen concentrations ($c > 3 \times 10^{-3}$ Mol/l). At this amount, the EPR lineshape cannot be described by a superposition of Lorentzians. This transformation can be caused by increasing d–d interactions, both between the PCs themselves and between PCs and paramagnetic oxygen molecules. However in the case of a 3-dimensional (3D) PC distribution, such transformation should not change the Lorentzian lineshape, which is characteristic of both exchange narrowing and dipolar broadening in a magnetically dilute system (8). The existence of the distant EPR wings, which fall off slower than the Lorentzian ones, can be explained by a 2D distribution of the PCs on the char surface. A high surface area (about 10² m²/g) typical of the chars under study (10) favors such a distribution.

The transformation of Lorentzian lineshape to a dipolar one with oxygen concentration increase indicates that the inequality [2a] becomes progressively invalid, and finally turns to $J \leq \delta_d \approx 10$ G. This suggests that adsorbed paramagnetic oxygen molecules disturb the PCs electron wave function, thus leading to a decrease of the exchange interaction between the PCs. As a result, the exchange narrowing breaks down and the 2D dipolar mechanism dominates.

The EPR lineshape in magnetically dilute d–d systems can be described by statistical theory with the use of the Anderson model (11). It was recently shown by Fel'dman and Lacelle (12) that the free induction decay (FID) in such systems with arbitrary dimensionality $D = 1, 2,$ or 3 of the PC distribution has the form

$$S(t) = S(0) \cdot \exp(-t/T_2)^{D/3}. \quad [3]$$

The EPR absorption lineshape is related to the FID through the Fourier transformation (8). In particular case of $D = 3$ one gets the well-known Lorentzian

$$g_L(\delta) = \frac{1}{\pi} \cdot \frac{T_2}{1 + (\delta T_2)^2}, \quad [4]$$

where δ is the frequency shift from the center of the line. The analytical expression for the EPR lineshape in the case of a 2D distribution is not available. The analysis shows that the distant wings at $D = 2$ fall off as $\delta^{-5/3}$, that is, slower than the Lorentzian wings. We successfully used the 2D dipolar lineshape to fit our experimental EPR spectra at an oxygen concentration of $c > 3 \times 10^{-3}$ Mol/l (see inset in Fig. 1). Thus, using the superposition of two Lorentzians at low oxygen concentration and the superposition of two 2D dipolar–dipolar lines at higher concentration we fitted the experimental EPR spectra in the whole range of the oxygen concentrations, with a precision equal to the signal-to-noise of the spectra.

The peak-to-peak EPR linewidth derivative δH_{pp} for both Lorentzian and 2D dipolar lineshapes is related to the T_2

parameter for both Lorentzian and 2D dipolar lineshapes,

$$\delta H_{pp}(\text{Lorentz}) = 1.155(\gamma T_2)^{-1} \quad [5]$$

$$\delta H_{pp}(2D) = 0.398(\gamma T_2)^{-1}, \quad [6]$$

where γ is the gyromagnetic ratio. One can see from Eqs. [5] and [6] that at a given T_2 value, the dipolar 2D line has a sharper central part and more intense distant wings than the Lorentzian one.

The theoretical formula for T_2 value caused by d–d interactions in a dilute 2D system was obtained in Ref. (12). However, only a perpendicular orientation of the external magnetic field relative to the plane containing PCs was considered. In our case of powdered chars, an averaging must be performed over all random orientations of the char surfaces. After averaging over all angles between the surface and the external magnetic field \mathbf{H} the following formula was obtained,

$$T_2 = (4.65 n_{2D}^{3/2} \hbar^2)^{-1}, \quad [7]$$

where n_{2D} is the PCs surface density, and \hbar is the Plank constant. More detailed theoretical consideration is published elsewhere (13).

Utilizing Eq. [7] one can estimate T_2 value in chars under study. Using experimental data for the “Peltogyne” sample—PC concentration, $4.7 \times 10^{19} \text{ g}^{-1}$; density, 2.2 g/cm^{-3} ; surface area, $100 \text{ m}^2/\text{g}$ —one gets $n_{2D} = 4.75 \times 10^{13} \text{ cm}^{-2}$ and $T_2 = 2.0 \times 10^{-9} \text{ s}$. This calculated T_2 value is in good agreement with the experimental data for centers B in Fig. 2b. As the concentration of oxygen increases and exchange narrowing between PCs in char disappears, the T_2 value asymptotically tends to $2.0 \times 10^{-9} \text{ s}$. Thus in accordance with the suggested model, the transverse relaxation at $c > 3 \times 10^{-3} \text{ Mol/l}$ is due to 2D d–d interactions between the free radicals.

Transverse relaxation of centers A , enriched with oxygen, could be governed by d–d interactions not only between the PC-themselves, but also with the nearby O_2 molecules, which are known to have orbital magnetic moments. Corresponding PC transverse relaxation rate progressively increases upon raising the oxygen concentration, and finally follows the law

$$T_2^{-1} \propto N_o^{3/2},$$

where, by analogy with Eq. [7], N_o is the surface density of the adsorbed O_2 molecules. One can see from Fig. 2b that such behavior does indeed take place. Utilizing Eq. [7] one can get $N_o \sim 1 \times 10^{14} \text{ cm}^{-2}$ at the atmospheric pressure.

Thus at low oxygen concentration, the exchange process between PCs dominates, leading to the observed Lorentzian EPR lineshape. As oxygen concentration increases above $3 \times 10^{-3} \text{ Mol/l}$, the paramagnetic oxygen molecules may progressively disturb the wave functions of PC and break the Heisenberg

exchange between them. As a result, the EPR linewidth tends to increase to the value determined by magnetic 2D dipole–dipole interaction.

Finally, it should be noted that most applications of the chars are in the liquid phase (aqueous biological media). The results of the present study are consistent with the data obtained previously in aqueous char suspensions (6); further investigation including detailed analysis of the EPR lineshape in aqueous systems is in progress.

V. CONCLUSION

The model is suggested to explain the molecular oxygen concentration effect on the evolution of the EPR spectrum of newly synthesized carbon-based chars. The following points form the basis of the model:

1. The paramagnetic organic free radicals in chars form two types of paramagnetic centers, differing by their distance to the adsorbed oxygen molecules. Each type of PC can be characterized by its own oxygen sensitivity and EPR linewidth.
2. At small oxygen concentration up to $3.0 \times 10^{-5} \text{ Mol/l}$ the EPR linewidth in chars is much narrower than that observed at atmospheric oxygen concentration. Intensive Heisenberg electron–electron spin exchange interaction between the radicals themselves is responsible for such an extremely narrow EPR linewidth.
3. With increasing oxygen concentration, the paramagnetic oxygen molecules start to break up the radical–radical exchange, which leads to EPR line broadening. When the oxygen exceeds $3.0 \times 10^{-3} \text{ Mol/l}$, the 2D dipole–dipole interactions between the paramagnetic centers come into play. This results in broadening as well as changes in the EPR line shape.
4. Over the whole range of oxygen concentration, the total amount of PCs remains constant, as measured by the integrated intensity of the experimental EPR line. This fact supports a model in which there is a mutual transformation of different types of paramagnetic species. The oxygen behavior of all EPR parameters is reversible.

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