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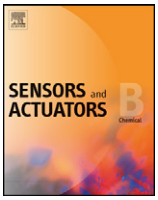

Data analysis and aging in phosphorescent oxygen-based sensors

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ABSTRACT

The stretched exponential analysis of the photoluminescence (PL) decay curves of the oxygen-sensitive dye Pt octaethylporphyrin (PtOEP) embedded in a polystyrene (PS) film and used in gas-phase oxygen, dissolved oxygen (DO), glucose, and lactate sensors is discussed. Light emitting diodes (LEDs) and organic LEDs (OLEDs) served as the pulsed excitation sources for the PL. Typically, the stretched exponential analysis resulted in excellent fits of the oxygen-quenched PL decay curves, superior to the single exponential analysis (including an offset) and other models, in particular at the higher oxygen levels. While some previous studies of gas-phase oxygen sensors analyzed the decay curves with a single value of the stretching factor β (which was not suitable in this work), and other studies used the product of a single exponential and a stretched exponential with a fixed β, in this study only the stretched exponential term was used with β as a variable. As a result, β was found to decrease with increasing O_2 concentration ($[O_2]$), from $\beta = 1$, i.e., a simple exponential decay, at gas-phase $[O_2] = 0$ and $[DO] = 0$. The effect of doping the PtOEP:PS films with 360 nm titania particles (which enhance the PL) on the data analysis was also examined. In general, the TiO_2 increased the PL decay time and β. The results indicate that a distribution of O_2:dye collision rates, induced by the microheterogeneity of the sensor films, is responsible for the non-exponential decay kinetics. The $[O_2]$-dependent β is possibly associated with shallow multiple quencher trapping sites in the PS matrix that affect the frequency of dye:O_2 collisions. The TiO_2 particles may possibly increase O_2 trapping at their surface, reducing the effective concentration of O_2 molecules that collide with the dye, and thus increasing the PL decay time and β. Additionally, the long-term stability, data analysis, and detection sensitivity of the DO sensor during and following one-year aging, with the sensing film constantly immersed in water, are described. The findings impact commercial PL-based DO sensors.

1. Introduction

Photoluminescence (PL)-based oxygen sensors have been studied extensively [1–21], and such devices, monitoring gas-phase and dissolved oxygen (DO), are available commercially. The PL-based sensors are advantageous over the electrochemical sensors due to attributes such as improved stability, lower maintenance, and less-frequent calibration. Moreover, issues common to electrochemical sensors, including oxygen consumption and electrode poisoning, are eliminated.

The PL-based oxygen sensors typically utilize an oxygen-sensitive dye embedded in a thin polymeric or sol–gel film. When the excited dye collides with oxygen molecules its PL is quenched with a dose-dependent decrease in the PL intensity I and decay time τ. Calibration lines and the oxygen level can be obtained using the Stern–Volmer (SV) equation

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV}[O_2] \tag{1}$$

where I_0 and τ_0 are the unquenched values and K_{SV} is the film- and temperature-dependent SV constant.

When using thin-film-based sensors, the ideal behavior described by Eq. (1) is often not obeyed [8,12–21]. This situation is usually due to microheterogeneity of the matrix and consequently, to luminophore molecules in sites that are not equally accessible to the quencher. Thus, several approaches have been suggested to modify Eq. (1). As an example, Eq. (1) was modified to include a sum of two or multiple exponential terms representing luminophore/site combinations with specific K_{SV} and fractional contributions that depend on the local environment of the luminophore [1–3]. Indeed, the use of a two-site model, with two discrete sets of quenching parameters, resulted in improved fits of I_0/I vs $[O_2]$ plots for Ru dyes in some polymer and sol–gel derived matrices [1,2,11]. Another model that resulted in improved fitting assumed that the deviation of the SV equation from linear-

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ity is due to the non-linear solubility of oxygen in the polymeric matrix [3,18–21]. It was shown that this model is mathematically equivalent to the multisite binding model [3].

Similar to the PL intensity, the PL time-resolved intensity decay kinetics was described as a sum of individual single exponential components with characteristic τ values and preexponential amplitudes [11]. In the foregoing approaches, obviously, the number of fitting parameters increased in comparison to the single exponential analysis. In another work [4], it was shown that a fit of the decay kinetics to a sum of exponentials for a Ru dye in various polymers results in an unreasonable dependence of the preexponential factors on the oxygen pressure. A distribution of relaxation rates, based on the interaction of the dye with its heterogeneous environment, was therefore proposed. This model required a smaller number of fitting parameters in comparison to the multi-exponential model. In another model [7], which resulted in a comparable decay function and was also developed to include the influence of the microenvironment on the PL decay time, it was assumed that the PL quenching due to luminophore–polymer matrix interactions depends on the distance between the luminophore and the nearest interacting polymer site. As such, the quenching rate of a given excited molecule is the sum of its distance-dependent interactions with a number of quenching sites. According to the authors [7], for the examples they provided, this model is physically and practically advantageous over the multi-exponential and rate-distribution models. It was simplified by Bossi et al. [9] who showed that the non-exponential PL decay of two Ru dyes embedded in polydimethylsiloxane (PDMS) was accurately described by the function

$$I(t) = I_0 \exp(-Bt^{0.5}), \tag{2}$$

i.e., a special case of the stretched exponential behavior [4,7,9,13,14,22–24] described below, where the stretching factor $\beta = 0.5$. Bossi et al. [9] suggested that this behavior was due to saturation of $[O_2]$ in the PDMS film, i.e., $[O_2]$ in the film was sublinear in the O_2 partial pressure of the surrounding gas. In all these examples, the single exponential analysis of the PL decay curves was inadequate even in the absence of the oxygen quencher. As shown below, the latter was not the case in the experiments presented here, where, in the absence of O_2, a single exponential analysis (that always included a background, i.e., an offset) resulted in an excellent fit to the PL decay curves.

The stretched exponential behavior

$$I(t) = I_0 \exp\left[-\left(\frac{t}{\tau_{\mathrm{kww}}}\right)^{\beta}\right] \tag{3}$$

is often used to describe dispersive processes in polymers. τ_{kww} is a characteristic value (kww refers to Kohlrausch–Williams–Watts, who applied the stretched exponential function to relaxation and scattering processes in disordered systems [22]).

The stretched exponential expression reflects a distribution of simple exponentials with different τ values and a specific distribution function $\rho(\tau)$.

$$I(t) = \int_0^{\infty} \exp\left(-\frac{t}{\tau}\right) \rho(\tau)\mathrm{d}\tau. \tag{4}$$

It is a result of the microheterogeneity in disordered solid matrices and that disorder is quantified by the deviation of the parameter β from unity [9]. It was shown to be exceptionally rewarding and insightful in the analysis of relaxation of a wide class of disordered systems and of atomic H diffusion in amorphous semiconductors [25,26].

The ensemble average $\langle\tau\rangle$ and the square root of the variance $\sigma^{1/2}$ of the decay-time distribution are determined from τ_{kww} and β [13]:

$$\langle\tau\rangle = \left(\frac{\tau_{\mathrm{kww}}}{\beta}\right) \Gamma(\beta^{-1}) \tag{5}$$

$$\sigma^{1/2} = \langle\tau\rangle\, w = \langle\tau\rangle \frac{[\beta\,\Gamma(2\beta^{-1}) - \Gamma^2(\beta^{-1})]^{1/2}}{\Gamma(\beta^{-1})} \tag{6}$$

where

$$\Gamma(x) = \int_0^{\infty} z^{x-1} \exp(-z)\mathrm{d}z \tag{7}$$

is the Gamma function and w is the relative (dimensionless) distribution width [13].

Besides the analysis by Bossi et al., where $\beta = 0.5$, an analysis using the product of a simple exponential and a stretched exponential successfully described the PL decay of Pd tetraphenyl-porphyrin (PdTPP) encapsulated in polymethylmethacrylate (PMMA) [13]. In that analysis, β varied from 0.73 to 0.79 over the first 10 h of measurements on their films.

In the present work, we describe the use of the stretched exponential analysis to obtain the (least squares) values of β and τ_{kww} for the PL decay curves of Pt octaethylporphyrin (PtOEP) embedded in polystyrene (PS) (PtOEP:PS), where the PL is quenched by either gas-phase O_2 or DO. From β and τ_{kww}, $\langle\tau\rangle$ and $\sigma^{1/2}$ are determined (see Eqs. (5) and (6)). We also include the analysis of 360 nm TiO_2 particle-doped PtEOP:PS films, since these particles enhance the PL up to 10-fold [17]. The analysis results in excellent fits for both undoped and doped films. It also shows that TiO_2 doping increases $\langle\tau\rangle$ and β, consistent with trapping of O_2 at sites induced by the TiO_2; such sites may prevent interaction of O_2 molecules with the PtOEP and hence increase the PL decay time. This is equivalent to a reduction in the effective concentration of O_2 that collides with the dye molecules, and consequently results in an increase in β. This analysis, in which the fitted parameters (besides the amplitude I_0 and the background (i.e., offset level) are τ_{kww} and β, resulted in better fits of the oxygen-quenched PL decay curves following pulsed excitation. More importantly, it provided insight into the nature of the microheterogeneity of the environment in which the PL quenching O_2 diffuses. Specifically, it was found to be consistent with a scenario in which the O_2 diffuses through a multiple-trapping-site system that affects the dye:O_2 collision rate. The analysis was used for gas-phase oxygen and DO sensors as well as for glucose and lactate sensors. The latter are based on monitoring oxygen following the oxidation reaction of glucose (lactate) in the presence of glucose (lactate) oxidase and oxygen [27–30]. Oxygen is consumed during the oxidation reactions, resulting in enhanced I and longer τ. The modified SV equation usable for monitoring these analytes when the reactions take place in a closed cell is given by [30]

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{\mathrm{SV}} \times \{[\mathrm{DO}]_{\mathrm{initial}} - [\mathrm{analyte}]_{\mathrm{initial}}\} \tag{8}$$

$1/\tau$ vs $[\mathrm{analyte}]_{\mathrm{initial}}$ is expected to be linear up to $[\mathrm{analyte}]_{\mathrm{initial}} \leq [\mathrm{DO}]_{\mathrm{initial}}$. At higher analyte concentrations, $1/\tau$ does not change by increasing the analyte concentration, since in sealed cells the DO is already completely consumed.

The paper presents also aging data for a DO sensor. While commercial oxygen-sensitive sensing films may be suitable for monitoring oxygen for one year, long-term aging studies of the oxygen-sensitive dye PdTPP in a PMMA film indicated a decrease of the average PL quenching rate by a factor larger than four during a nine-month aging period [13]. Previously, some sol–gel sensor materials with embedded tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) ($Ru(dpp)_3$) demonstrated long-term stability over an 11-month period [11]. However, Pt- and Pd-porphyrins, with their longer τ_0 and consequently