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Application of frequency spectroscopy to fluorescence-based oxygen sensors

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Abstract

This study addresses the problem of specification of physical models for quenched-fluorescence-based oxygen sensors by analysing their complex frequency response (both intensity and phase signals) at different working frequencies and oxygen concentrations. Two common physical models of active medium, the single-exponential model with non-linear oxygen solubility and the double-exponential model were considered, with the example of heterogeneous PtOEPK-PS-based oxygen sensor. It was found that within the limits of experimental errors, the non-linear oxygen solubility models describe more adequately experimental data for the sensor. Model parameters were defined and analysis of the sensors system performance at different working frequencies and oxygen ranges was made.

Keywords: Frequency spectroscopy; Oxygen sensors; Quenched-fluorescence

1. Introduction

Quenched-fluorescence oxygen sensors have emerged as highly versatile and useful technology [1–3]. They are gaining active use in various areas and applications, including biomedical, packaging, environmental, process control and biosensing [4–9]. This sensing approach allows reversible, non-chemical, contact-less monitoring of molecular oxygen and processes which consume or release oxygen [3]. Solid-state sensor active elements used in such systems usually comprise heterogeneous materials which display complex photophysical and quenching behaviour in conditions of their use [10–13]. Therefore, investigation of processes taking place in the sensor, theoretical description of sensor behaviour and determination of its working characteristics are important analytical tasks. This is essential for accurate determination of oxygen concentration/partial pressure (p_{O_2}).

The majority of lifetime-based oxygen sensor systems operate at constant excitation frequency, at which sensors are calibrated by performing sets of phase or intensity measurements at several temperatures and p_{O_2} standards [10–17]. Such type of sensor characterisation rarely permits precise definition of sensor physical model and determination of its parameters. For example, the two commonly used double-exponential and non-linear solubility sensor models, which are very different in physical terms, both provided similar accuracy in oxygen determination when using phase calibrations at a single frequency [10,14–17]. Furthermore, as shown in Ref. [14], these models can be converted into each other by algebraic transformation and therefore cannot be distinguished using such calibrations. Strictly speaking, sensor parameters defined from calibrations at one working frequency cannot be simply transferred to other frequencies.

Frequency spectroscopy is a powerful method, which is used in fluorometry [18] and also in electrochemistry and material science [19–21]. It allows a more detailed characterisation of samples by analysing signals in complex values (e.g. amplitude and phase for fluorescence or real and imaginary components for impedance) along a certain frequency range. Compared to calibrations at a single frequency, frequency spectroscopy provides greater amount of information for the same number of points (oxygen standards). Therefore,

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one can expect it to provide a more accurate specification of sensor physical model, reduced effects of experimental errors and a more accurate oxygen quantification.

In this study, we describe application of frequency spectroscopy to perform characterisation of the solid-state phosphorescent oxygen sensors. Sensor frequency response in complex values was obtained for PtOEPK-PS-based sensor on porous support [13] and the phosphorescence phase detector with multi-frequency measurement capabilities [13,22]. Sensor signals (intensity and phase angle) were measured at different frequencies and several oxygen standards. They were then analysed using the two common sensor models, the double-exponential and non-linear solubility models aiming to differentiate the models and determine sensor working characteristics.

2. Theory

2.1. Non-linear complex fitting procedure

To perform the fitting of the sensor frequency response described in complex values, a modified algorithm previously used for approximation of sensor phase or intensity calibrations at a single frequency [14,15] was employed. In this case, specification of the model of active medium was performed by means of complex non-linear fitting procedure similar to Refs. [18,20,21]. According to this method, vector of model parameters $\vec{P} = (p_1, p_2, \ldots, p_k)$ was determined by minimising the deviations between experimental Se_i and calculated Sc_i complex-valued readings (for example imaginary and real parts) at each frequency point. A sum of weighted squares of these deviations at each i-frequency point ($i = 1, \ldots, N$) was used as target function T, where weighting coefficients w_i^a and w_i^b served to reduce the effects of measurement errors and noise.

$$T = \sum_{i=1}^{N} \{w_i^a \{\mathrm{Re}(Se_i) - \mathrm{Re}[Sc(f_i, \vec{P})]\}^2 + w_i^a \{\mathrm{Im}(Se_i) - \mathrm{Im}Sc[(f_i, \vec{P})]\}^2\} \qquad (1)$$

In the simplest case, w_i^a and w_i^b were equated to unity (unity-weighted or unweighted target function). If S^a and S^b values varied significantly in the region of approximation, then reciprocal standard deviations $(\sigma_i^a)^{-2}$ and $(\sigma_i^b)^{-2}$ were taken as weighting coefficients. If these deviations appeared to be unreliable or were missing, proportional estimates of these deviations $\sigma_i^a = g\,\mathrm{Re}(Se_i)$ and $\sigma_i^b = g\,\mathrm{Im}(Se_i)$ with $g = 1$ were used.

In contrast to approximation error for real numbers, for which metric is a simple modulus of difference between numbers, metric for complex values determines distance between the two points on complex plane. This distance is calculated depending on coordinate system applied. For orthogonal system with real Re(S) and imaginary Im(S) parts as well as for polar system with modulus $|S|$ and phase angle φ coordinates, the distance represents absolute distance D between the two points on the plane and calculated as:

$$\begin{aligned} D &= |Se - Sc| \\ &= \sqrt{(\mathrm{Re}(Se) - \mathrm{Re}(Sc))^2 + (\mathrm{Im}(Se) - \mathrm{Im}(Sc))^2} \\ &= |Se| \left| 1 - \frac{|Sc|}{|Se|} e^{j(\varphi_c - \varphi_e)} \right| \end{aligned} \qquad (2)$$

For polar system with logarithmic radius scale and radian phase, this distance is calculated as:

$$\begin{aligned} L_s &= \sqrt{(\ln|Se| - \ln|Sc|)^2 + (\varphi_e - \varphi_c)^2} \\ &= \sqrt{\left(\ln\left|\frac{Se}{Sc}\right|\right)^2 + (\varphi_e - \varphi_c)^2} \end{aligned} \qquad (3)$$

which defines semi-logarithmic metric L_s. Other coordinates can also be used to map sensor readings. However, it is important to choose a particular metric which gives the most clear representation of sensor behaviour, since then fitting procedure performed in this metric will provide the best agreement between the experimental and fitted data.

Proportional weighting can be obtained by normalising D metric (2) components for modulus (d-weighting) of experimental complex-valued sensor response:

$$d = \left| \frac{Se - Sc}{Se} \right| = \left| 1 - \frac{|Sc|}{|Se|} e^{j(\varphi_c - \varphi_e)} \right|. \qquad (4)$$

One can show that if the difference between experimental and fitted data points is small, proportional weighting becomes close to semi-logarithmic metric (3).

The above algorithm was applied to complex-valued frequency response of the oxygen sensor (intensity and phase angle readings) for each oxygen standard. This allows determination of sensor model parameters describing its frequency behaviour and oxygen dependence of these parameters. As before [14,15], to compare errors for the experiments with different number of data points and to assign more physical meaning to the target function, mean square of local error (Mae_i) was used:

$$MAe = \sqrt{\frac{\sum_{i=1}^{N} {Mae_i}^2}{N}} \qquad (5)$$

determined for experimental points ($i = 1, \ldots, N$) in each of the metrics (2)–(4). This parameter defines the quality of approximation as mean square error at each frequency point, interpreted as standard error. Different metrics (2)–(4) used to evaluate target functions for each set of experimental data ensured finding of global minimum and gave estimation of scattering of model parameters.