Luminescence-based oxygen sensing with ruthenium(II) complexes

Ru(II) ----N (CIO₄*)₂

n- alkvl

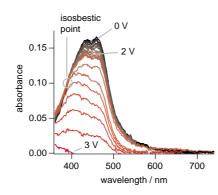
 $ETH^{T} 3001 n = 3$ $ETH^{T} 3003 n = 8$

Most oxygen sensors which are used today determine oxygen by electrochemical (Clark electrodes) or optical methods (quenching of a dye's luminescence). Clark electrodes have found widespread industrial use but do not provide a universal solution, especially for small probes and turbulent flows. Therefore alternatives are needed.

Optical sensors for oxygen use a dye whose luminescence is efficiently quenched in the presence of oxygen, i.e. the excited state of the dye molecule is deactivated by an oxygen molecule without any light emission. A very high selectivity to oxygen is achieved because only few other compounds fulfil the electronic requirements needed for such a deactivation. To obtain an analytically useful signal either the luminescence intensity or the life time of the excited state can be monitored, both decreasing with increasing oxygen concentration.



The flow-through cell is one of the components of the measurement set-up which needs to be optimized.



Spectroelectrochemistry is one of the methods to find out more about the long-term bleaching behavior of ETH^T 3001

Immobilisation of the dye is usually done by incorporating it into a polymer layer such as polystyrene. The sensor selectivity and sensitivity can be tuned by the polymer's solubility and permeability properties to gases.

Improving long-term stability

Our aim is to improve, among other important characteristics, the stability of the oxygen sensors. This can be achieved by using more lipophilic complexes, which are not washed out from the membrane by aqueous samples. A different lipophilicity furthermore significantly broadens the range of possible membrane materials, thus allowing more options for improving the membranes in terms of sterilisability and biocompatibility.

For this purpose, we have synthesised lipophilic tris(4,7-bis-(4'-n-alkyldi-

phenyl)-1,10-phenanthroline)-ruthenium(II) perchlorates with n=3, and 8 (ETH^T 3001 and 3003). We found that dye characteristics, such as quantum yield, luminescence life time as well as the absorption and emission spectra remain essentially unchanged when comparing ETH^T 3001 with the widely used, but less lipophilic tris(4,7-diphenyl-1,10-phenanthroline) ruthenium(II) perchlorate. Excitation and emission of the complexes are in the visible spectral range with 460 and 620 nm respectively.

Response times of the sensor are below 1 s in gases and below 30 s in water for polystyrene membranes. A reliable, automated measurement set-up is necessary to actually assess long-term stability. Light bleaching has been found to be the main degrading force for the membrane and is therefore investigated in detail.

Project highlights

- Examination of long-term behaviour of sensor membranes
- Sterilisability of membranes
- Photo-/electrochemistry of the dye and the sensor membrane
- Measurement automation with LabVIEW

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