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Application of phosphorescent oxygen sensors in in-package dielectric barrier discharge plasma environment

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ABSTRACT

Dielectric barrier discharge plasma treatment of two different types of phosphorescent oxygen sensors under different in-package gas mixture has been studied. Commercial Optech™-O_2 platinum and microporous polypropylene (PP) membrane sensors impregnated with platinum benzoporphyrin (PtBP) dye were found effective for oxygen sensing when DBD plasma treated under modified atmospheric conditions. When treated under DBD air plasma, PP sensors were largely degraded and found incompatible with the plasma processing. Although some changes in the lifetime signals were observed after air plasma treatment, Optech™-O_2 platinum sensors were found effective as oxygen sensors. This study indicates that in-package gas composition of food products plays an important role in selection of right intelligent optochemical sensors for plasma processing.

Industrial Relevance: In-package cold plasma processing is emerging as a novel and innovative approach for the decontamination of food products with significant potential for commercial application. This paper studies the compatibility of phosphorescent oxygen sensors with this technology. This study demonstrates that the package gas composition has huge impact on the accuracy and usability of sensors. The work described in this research is relevant to all food industries which uses intelligent sensors for monitoring gas composition.

1. Introduction

Non-thermal plasma (NTP) has been used for decades in the packaging industry for surface modification and functionalization of various polymers. The term 'plasma' refers to a partial or completely ionized gas essentially composed of photons, ions, free electrons and atoms in their fundamental or excited states possessing a net neutral charge (Misra, Tiwari, Raghavarao, & Cullen, 2011). Depending upon the relative energy levels of electron and constituent heavy species, plasma can be either thermal or non-thermal. Unlike thermal plasma, NTP has temperature disequilibrium between electron and heavier species with relatively lower electron density of less than 10^{19} m^{-3} (Tendero, Tixier, Tristant, Desmaison, & Leprince, 2006). The application of non-thermal plasma for food decontamination has been previously reviewed by Niemira (2012) and Misra et al. (2011)

Non-thermal plasmas at atmospheric pressures can be generated using several techniques. Dielectric barrier discharge (DBD) is one such method which offers versatility in its mode of operation and system configuration (Pankaj, Misra, & Cullen, 2013). In the recent years, non-thermal plasma has also drawn interest of various researchers as novel in-package food decontamination technology. This approach involves generation of NTP inside a sealed package by placing it between a high voltage and a ground electrode. Upon exposure to a sufficiently high voltage, the gas contained in the package gets ionized, generating significant amounts of reactive species, which in turn leads to decontamination of the enclosed products. The effectiveness of this approach for microbial decontamination has been already reported by Connolly et al. (2013); Ziuzina, Patil, Cullen, Keener, and Bourke (2013) and Patil et al. (2014). Based on the approach various studies has also been reported for non-thermal plasma treated food products like spinach (Klockow & Keener, 2009), fish (Chiper, Chen, Mejlholm, Dalgaard, & Stamate, 2011), tomato (N. N. Misra, Keener, Bourke, Mosnier, & Cullen), strawberry (Misra et al., 2014) and meat (Rød, Hansen, Leipold, & Knøchel, 2012). The effect of non-thermal plasma on the food packaging material has also been reviewed (Pankaj, Bueno-Ferrer, Misra, Milosavljević, et al., 2014) and reported on different polymers like polyethylene, polypropylene, polystyrene and biodegradable films based on polylactic acid (Pankaj, Bueno-Ferrer, Misra, O'Neill, et al., 2014a, b), zein (Pankaj, Bueno-Ferrer, Misra, Bourke & Cullen,

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2014), caseinates (Pankaj, Bueno-Ferrer, Misra, O'Neill, et al., 2014c) and starches (Pankaj et al., 2015).

Since non-thermal plasma has also shown its potential application with various food products in which intelligent packaging systems are used, it became important to analyze the effectiveness of intelligent packaging systems in association with DBD plasma treatments. Intelligent packaging can be defined as a packaging system that is capable of carrying out intelligent functions (such as detecting, sensing, recording, tracing, communicating, and applying scientific logic) to facilitate decision making to extend shelf life, enhance safety, improve quality, provide information, and warn about possible problems (Yam, Takhistov, & Miltz, 2005). Package integrity is an essential requirement for the maintenance of quality and safety of food products in modified atmospheric packaging (MAP) and optical solid-state gas sensors offer an alternative, non-invasive approach to traditional destructive techniques to determine the package integrity (Vanderroost, Ragaert, Devlieghere, & De Meulenaer, 2014). The most important gases in MAP products are oxygen and carbon dioxide and their headspace partial pressures serve as useful indicators of the quality status of food products (Kerry, O'Grady, & Hogan, 2006). Among these, oxygen indicators are the most common for food packaging applications, because oxygen in air can cause oxidative rancidity, color change, and microbial spoilage (Yam et al., 2005). In this study, two different types of phosphorescent solid-state oxygen sensors were used under atmospheric air and modified-air (30% CO_2 + 70% N_2) conditions for analyzing the compatibility of these oxygen sensors with novel in-package DBD plasma treatment.

2. Experimental

2.1. Materials

The non-woven microporous polypropylene sheets (Type FS2192i, thickness 80 ± 20 mm, mean pore size = 17 mm, and fibre size = 8–12 μ) were obtained from Freudenberg, UK; Platinum (II)-benzoporphyrin dye (PtBP) - from Luxcel Biosciences (Cork, Ireland); tetrahydrofuran (HPLC grade) - from Sigma-Aldrich, and N_2 and O_2 gases (99.999% purity) from Irish Oxygen (Ireland). Commercial PET/PE trays (150 mm × 150 mm × 35 mm) were from Holfield plastic, Ireland. Anti-fog coated BOPA/PE/EVOH/PE films (thickness = 0.043 mm) were purchased from DAZA, Spain and used as top film for tray sealing. For MAP, pre-blended 30% CO_2 + 70% N_2 gas mixture were from BOC, Ireland. Optech™-O_2 platinum sensors (sensor A) were purchased from Mocon, (Minneapolis, USA). These sensors were stored at room conditions and used without any further treatment.

For the PP sensors (sensor B), a solution of PtBP dye 70:30 THF/H_2O (0.03 mg/ml) was prepared (Kelly, Toncelli, Kerry, & Papkovsky, 2014) and 8 ml of the solution was placed in each 15 ml disposable vial (Sarstedt). Strips of PP membrane (24 mm × 12 mm) were placed in the solution ensuring strips were immersed fully in solution. The vials were then capped and incubated at 65 °C for 1 h. The samples were extracted, washed with water and air-dried for 4 h. Subsequently, the sensor strips were incubated in a dry oven at 70 °C for 16 h.

2.2. In-package plasma treatment

The details of the DBD plasma generation system has been described elsewhere (Pankaj, Bueno-Ferrer, Misra, O'Neill, et al., 2014a, b, c). Briefly, the DBD plasma is generated using a step-up transformer (Phenix Technologies, Inc., USA) regulated by a variac between two circular aluminium plate electrodes (outer diameter = 158 mm) over two dielectric barriers (Perspex: 10 mm, polypropylene: 2 mm). Oxygen sensors were sealed in the trays with atmospheric air and modified air and placed between the electrodes (Fig. 1). Based on our previous studies for food decontamination, sensors were treated at 80 kV for 5 min and each experiment was performed in triplicate. It should also be noted that the entire package itself served as an additional dielectric barrier. Control sensors were also prepared in the same way except the DBD plasma treatment for both sensors at both gaseous environments. All the sensors were stored at room temperature and analyzed within 48 h.

2.3. Sensor characterization

All the oxygen sensors were screened for the phosphorescence intensity and lifetime signals were recorded with a handheld instrument Optech™ (Mocon, Minneapolis, USA). The sensors were placed in a clear 20 ml polystyrene vial (Sarstedt, Ireland). Sensors phosphorescence intensity and lifetime (μs) were measured in both air (21 kPa O_2) and N_2 (0 kPa O_2). Each sensor strip was measured three times in different locations and average values were reported.

For sensor calibration standard O_2-N_2 gas mixtures (0–100 kPa O_2) produced using a precision gas mixer (LN Industries SA, Switzerland) were pumped through a flow cell with a glass window through which an O_2 sensor was interrogated with the Optech™ instrument. The flow cell was submerged in a circulating water bath (Julabo) keeping the window and probe above the water level to equilibrate the gas to the correct temperature (Fig. 2). Sensor A was calibrated at 21, 10, 5, 2, 1 and 0 kPa O_2 while sensor B was calibrated at 100, 21, 10, 5, 2 and 0 kPa O_2.

To analyze the effect of humidity on the sensors, both the sensors were also calibrated in the humid gas condition. In this case, the gases were purged through a glass jar filled with water and were then used to calibrate the sensors with the same setup as discussed before. Both the sensors were also analyzed at three different temperatures (10, 20 and 30 °C) to characterize the effects of temperature on the sensor phosphorescence intensity and lifetime signals.

In order to investigate the reversibility and response time, both the oxygen sensors were exposed to alternating streams of pure N_2 (0 kPa O_2) and air (21 kPa O_2) and the phosphorescence intensity was measured. The response ($t_{90}\downarrow$) and recovery ($t_{90}\uparrow$) times were denoted as the time required for the phosphorescence intensity to decrease and

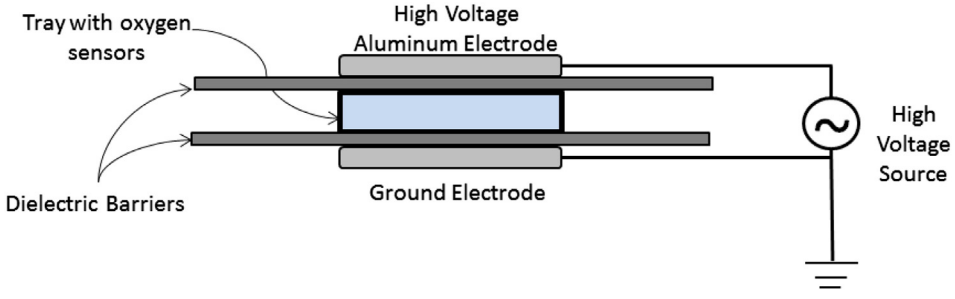

Fig. 1. Schematic of the experimental set-up employed for DBD plasma treatment of oxygen sensors.

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