Chemical Sensors Based on Surface Plasmon Resonance in a Plastic Optical Fiber for Multianalyte Detection in Oil-Filled Power Transformer

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Abstract. The combination of a D-shaped plastic optical fiber (POF) and a Molecularly Imprinted Polymer (MIP) receptor is an effective way to obtain a highly selective and sensitive surface plasmon resonance (SPR) optical platform, especially suitable for the detection of chemical marker in the oil of Power Transformers. In this work Authors present the preliminary results for determination of two important analytes, dibenzyl disulfide (DBDS) and furfural (2-FAL), whose presence in the transformer oil is an indication of underway corrosive or ageing process, respectively, in power transformers. The low cost of the POF-MIP platforms and the simple and modular scheme of the optical interrogation layout make this system a potentially suitable on-line diagnostic tool for power transformers.

Keywords: Dibenzyl disulfide · Furfural (furan-2-carbaldehyde) · Molecularly imprinted polymers · Plastic optical fibers · Power transformers

1 Introduction

Oil-filled power transformers are a key component of a Transmission and Distribution (T&D) network. Their failure can have relevant impact on maintenance costs due to out-of-services. Nowadays the increasing energy peak demand and its timing change can often expose power transformers to irregular stresses and/or overloads, that can compromise their long term integrity.

The availability of reliable and potentially low-cost sensors to be used as diagnostic tools for detecting ageing and failures of these components is of significant interest to improve management of the electric power system assets. In particular, for oil-filled transformers, the on-line continuous detection of chemical parameters (Dissolved Gases and chemical agents) in the insulating oil could provide an early warning of

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incipient failures (partial discharges, over temperature, hot spot) or of occurring accelerated aging on dielectric parts of transformers.

Surface Plasmon Resonance (SPR) based Plastic Optical Fibers (POF) sensors are good candidates for an on-line detection of different diagnostic markers directly in oil environment. This methodology potentially allow to overcome problems, foreseen by current practices, of periodical collections of oil samples from the transformer and application of more expensive and time-consuming standard analysis (by gas chromatography for instance).

The SPR is an optical phenomenon that appears at a metal-dielectric interface, widely used in a large number of sensors for label-free detection [1–4]. The Kretschmann configuration is widely used in practice, but the setup usually require expensive optical equipment. Incorporating optical fiber makes it possible to reduce the sensor cost and dimensions, with the possibility to integrate the SPR sensing platform in telecommunication systems [5–8]. Using a molecularly imprinted polymer (MIP) layer as an artificial receptor, the rapid and selective detection of different analytes in aqueous matrices has been demonstrated [9, 10]. Also, MIP-POF-SPR optical platform has been demonstrated to be potentially useful for the determination of 2-furaldehyde (2-FAL) directly in transformer oil, without any previous extraction procedure [11].

MIPs are synthetic receptors obtained by molecular imprinting methods, presenting a number of favorable aspects for sensing in comparison to bioreceptors, as for example antibodies, including high stability, reproducibility and low cost. They are porous solids containing specific sites interacting with the molecule of interest, according to a "key and lock" model [12]. Indeed, a distinctive feature of MIPs, in comparison with other receptors, is the selectivity. Moreover, the polymer layer may contain a relatively high density of recognition elements, included in a three-dimensional matrix, which should help the recognition by SPR even for relatively low molecular mass molecules.

In this work, as a case-study, we experimentally analyse the behavior of a newly developed POF-MIP-SPR multichannel sensor system, specialized for simultaneous and selective detection of dibenzyl disulfide (DBDS) and 2-furaldehyde (2-FAL) in transformer oil.

2 Optical Sensor System

The fabricated optical sensor system was realized removing the cladding of a plastic optical fiber along half the circumference, by mechanically polishing the plastic optical fiber without jacket embedded in a resin block, spinning on the exposed core a buffer of Microposit S1813 photoresist, and finally sputtering a thin gold film using a sputtering machine [13].

The chosen plastic optical fiber has a PMMA core of 980 μm and a fluorinated polymer cladding of 20 μm, the gold film is 60 nm thick and the thickness of the photoresist buffer layer is about 1.5 μm. The realized sensing region is about 10 mm in length (see Fig. 1).

The gold film so obtained presents a good adhesion to the substrate, verified by its resistance to rinsing in de-ionized water, and it is also easy to functionalize with bio/chemical receptors.

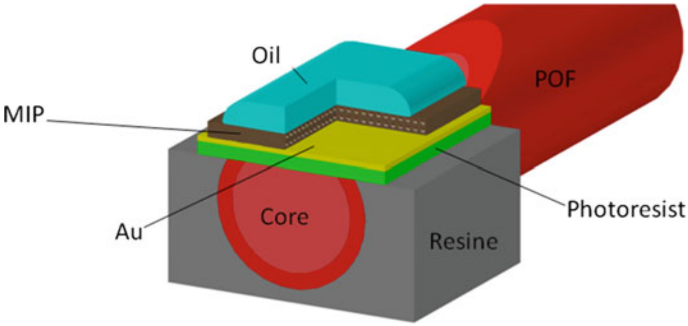

Fig. 1. Optical chemical sensor based on D-shaped POF

The experimental measurements for the characterization of the SPR-POF sensors have been previously carried out in different ways, i.e. spectral and amplitude mode. In this work we have used a particular setup based on the spectral mode configuration. It consists of a halogen lamp, a beam splitter (50/50) illuminating simultaneously the two optical chemical sensors, with different MIP (see Fig. 2a), and two identical spectrometers. The here used halogen lamp exhibits a wavelength emission range from 360 to 1700 nm, while the spectrum analyzer detection range was from 330 to 1100 nm. Two spectrometers were finally connected to a computer (see Fig. 2b).

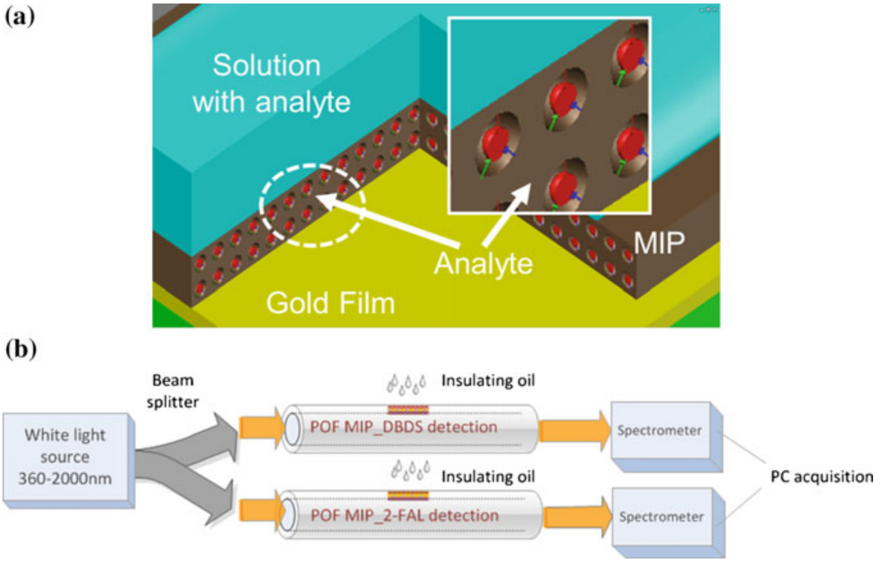

Fig. 2. **a** Zoom of the sensing area. **b** Schematic view of the experimental setup based on two POF-MIPs sensors for different analytes

3 The Sensitivity in Spectral Mode Operation

In SPR sensors with spectral interrogation, the resonance wavelength (λ_{res}) is determined as a function of the refractive index of the sensing layer (n_s). If the refractive index of the sensing layer is altered by δ_{ns}, the resonance wavelength shifts by $\delta\lambda_{res}$. The sensitivity (S_n) of an SPR sensor with spectral interrogation is defined as [13–15]:

$$S_n = \frac{\delta \lambda_{res}}{\delta n_s} \left[\frac{nm}{RIU}\right] \tag{1}$$

Owing to the fact that the vast majority of the field of an SPW is concentrated in the dielectric, the propagation constant of the SPW is extremely sensitive to changes in the refractive index of the dielectric itself. This property of SPW is the underlying physical principle of affinity SPR bio/chemical sensors.

In the case of artificial receptors, as molecular imprinted polymers (MIPs), the polymeric film on the surface of metal selectively recognizes and captures the analyte present in a liquid sample so producing a local increase in the refractive index at the metal surface. The refractive index increase gives rise to an increase in the propagation constant of SPW propagating along the metal surface which can be accurately measured by optical means. The magnitude of the change in the propagation constant of an SPW depends on the refractive index change and its overlap with the SPW field. If the binding occurs within the whole depth of the SPW field, the binding-induced refractive index change produces a change in the real part of the propagation constant, which is directly proportional to the refractive index change.

The chemical sensor's sensitivity (S) is defined as the shift in resonance wavelength per unit change in analyte concentration [16]:

$$S = \frac{\delta \lambda_{res}}{\delta C_{analyte}} \left[\frac{nm}{M}\right] \tag{2}$$

4 Experimental Results

Measurements were simultaneously carried out on two SPR-POF-MIP optical chemical sensors based on different MIP receptors: one for dibenzyl disulfide (DBDS) and one specific for furfural (2-FAL). A rapid and selective detection of these analytes is, actually, very important for an on-line control of oil in transformers to prevent their damages and/or failure.

Samples were obtained by dissolving the analyte in a mineral oil (Nytro Libra) widely used for power transformers, which does not contain DBDS and 2-FAL and is also used as a blank.

All the measurements were carried out by dropping 30 µl of the liquid sample (oil with analyte) directly over the two POF-MIPs sensor platform, which were maintained in horizontal position. Steady state wavelength shift were obtained after 3 min incubation.

Several plasmonic resonances were observed in the considered wavelength range (300–1100 nm) of the transmission spectra, when the binding interaction occurs between MIP and the analyte under investigation [9–11]. In this preliminary analysis only the red-shift of the SPR resonance (in the wavelength range 700–820 nm) will be taken into account hereafter.

Figures 3 and 4 report some preliminary results of DBDS and 2-FAL detection in transformer oil samples, respectively. They clearly show that the resonance wavelength is shifted to higher values (red shifted) when the DBDS (Fig. 3) and 2-FAL (Fig. 4) concentration increases, indicating that DBDS and 2-FAL effectively combines with MIP from the oil matrix.

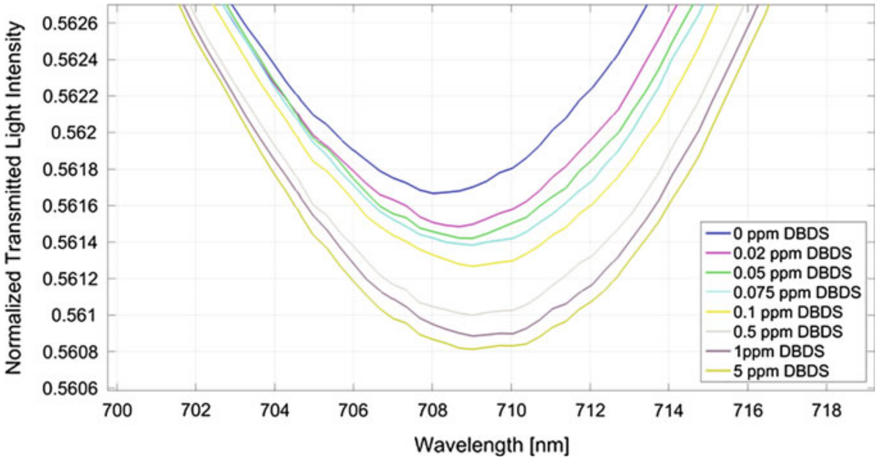

Fig. 3. Zoom of experimental SPR transmission spectra for different DBDS (ppm) in transformer oil

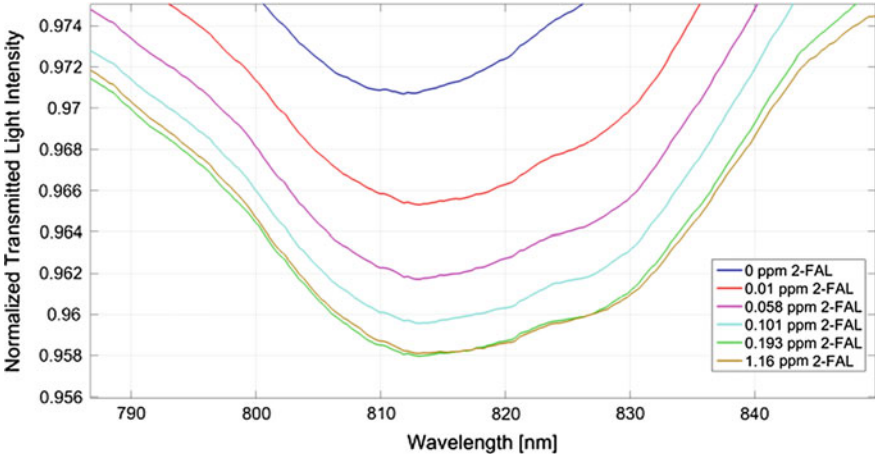

Fig. 4. Zoom of experimental SPR transmission spectra for different 2-FAL (ppm) in transformer oil

5 Conclusions

Preliminary experimental results on a multichannel chemical SPR sensor, for the detection of two markers (DBDS and 2-FAL) directly in transformer oil, have demonstrated an attractive feature in industrial application. In particular, for oil-filled transformers, the frequent control of chemical markers in the insulating oil could provide an early warning of incipient failures (partial discharges, over temperature, hot spot) or of occurring accelerated aging on dielectric parts of transformers [17–21].

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