Long period grating pair chloride ion sensor for early corrosion prevention

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Abstract. A novel approach to chloride ion monitoring in aqueous solutions using a long period grating (LPG) pair is reported, with the LPG pair used (LPGP) comprising two 2.5dB single LPGs and a physical centre-to-centre separation of around 30mm. An ultra-violet excimer laser was used to create the pair through a 250µm amplitude mask. The refractive index change due to the presence of the chloride ion (from an aqueous NaCl solution) was monitored, with the sensor having previously been calibrated using solutions of known refractive indices (RIs). A cross-comparison with the response of a single LPG (LPG1) under similar testing conditions was also carried out, and the results have shown that the LPGP could measure a RI change of ±0.003, achieving an improvement in the precision obtained (by ~ 6 times) using a single LPG. The focus of the work is on the underpinning technology for early stage corrosion monitoring (and indeed prevention) in structures, arising due to salt and water ingress.

1. Introduction
A major factor in the corrosion and degradation of many environmental structures is the penetration of chloride ions in aqueous solution [1]. Conventional sensor techniques [2] often are unsuitable for early corrosion detection or for measurand-specific monitoring for a variety of reasons and thus new approaches are being sought. Optical fibre-based techniques have been reported in this area, but often in systems needing expensive optical components (as in the case of the fluorescence-based systems) or showing irreversibility (as in the case of the absorbance-based sensor systems) [1]. Grating based systems, using the familiar Fibre Bragg Gratings (FBGs) and more recently Long Period Gratings (LPGs) have been reported [3,4] in these sorts of applications. However, using LPG pairs can be preferential to single LPGs, in terms of the sensor resolution due to the presence of sharp Mach-Zehnder interference fringes [5], supported by previous results from some of the authors [6]. In this study, work has been conducted using LPG pairs (LPGPs) to develop sensors to monitor small quantities of chloride ions [6] in aqueous solutions, which can operate under harsh environmental conditions. The sensor operates using various concentrations of NaCl where a refractive index (RI) change is monitored, following prior calibration against known NaCl concentrations and thus to detect the presence of small quantities (250 ppm) of chloride ions [6].
A number of previous investigations have been carried out into the performance of a single LPG-based sensor fabricated in single mode fibres to monitor various NaCl concentrations [3,7 and 8] but the LPG sensors have often not been effective when lower NaCl concentrations, up to 0.1g per 100ml, are considered. Extrapolation methods have been used instead to determine the potential sensor response at such low concentrations. Work by Scaria et al. utilizing a single LPG fabricated on a multimode plastic clad silica fibre with the cladding removed has been reported [6] and the scheme discussed could be used to detect chloride ion concentrations as low as few parts per billion. However, the main drawback is that the fibre sensor cladding layer is removed, making it fragile and not well suited for use outside the laboratory.

2. Sensor fabrication aspects of the LPGs and the LPG pairs

This work uses LPG pairs (in preference to either FBGs or single LPGs) where, as the separation increases, a higher number of sharper interference fringes is obtained [5]. A further advantage is that the smaller separation between the single LPGs allows the sensing region (the stripped fibre between the LPG gratings) to be smaller and thus higher precision in the positioning of the active region is possible, with the reduced LPG separation allowing the fibre to be mechanically stronger.

The effect of the RI change on a LPG pair with an LPG separation of 10cm was studied by Han et al. at several distinct values of RIs: 1.0, 1.4, 1.45, 1.458, and 1.69 [9]. Further work by Mishra et al. allowed the study of the performance of a LPG pair, using two mechanically induced long period gratings separated by 16cm, for various NaCl concentration changes of 5g, 10g, 15g and 20g per 100ml [10]. The results obtained showed a relatively poor resolution for the sensor overall, where there was a change in the optical power transmitted in response to the RI change, but with no detected wavelength shift. A high sensitive refractometer using a LPG pair with a 20cm separation between the LPGs has also been reported. The refractometer thus created was able to detect RI changes of up to 1.8 x 10^-6 using a heterodyne detection technique [11].

The grating sensors used in this work (a LPGP – using a relatively short overall length of ~3.7 cm – and an LPG labelled LPG1) were fabricated on boron germanium co-doped fibre with a numerical aperture, diameter, and cut-off wavelength of 0.14, 125.1µm, and 1246nm respectively. The two LPGs forming the pair were fabricated on the same fibre with no splicing involved. To do so, an ultra-violet KrF excimer laser (Braggstar 500) was used, with a pulse energy of around 8mJ and a frequency of 100Hz (via a 250µm amplitude mask). The transmission spectra (a typical spectrum is shown in Figure 1) are detected using an Optical Spectrum Analyser (OSA- type HP86140A), when illuminated by a low-power light from a broadband source (LS-1 Tungsten Halogen Lamp, supplied by Ocean Optics).
Figure 1: Transmission spectrum of LPG1. The highest order stop band (SB$_h$) monitored through the experiments is highlighted

3. Experimental set up and results

The sensors initially were calibrated over a wide range using the standard approach of Cargille RI liquids with the experimental setup used is as shown in Fig. 2. In preparation, each sensor was flushed with either water or isopropanol alcohol before immersion in the Cargille liquids (or later the NaCl solutions) to eliminate errors in the measurements as a result of residues that may adhere to the sensing element. The experiments were conducted in a controlled room temperature environment with samples adequately equilibrated before use.

When the LPGP sensor was immersed in any of the solutions used, a transient wavelength shift of the pit under study was monitored. This shifted to an initial lower wavelength (a blue shift), followed by a backward shift (a red shift) to settle to a final wavelength value. The overall wavelength change monitored is a blue shift (i.e. toward lower wavelengths). This behaviour was observed in all the experiments which were conducted and found to be repeatable. The average time for the LPGP to stabilize to the final wavelength value was around 3-5 minutes.
The induced wavelength shifts of the LPGP and LPG1 obtained over a wide range of changes of RI values are shown in Fig. 3. It was noticed that the interference fringes of the LPGP were lost when RI liquids of values from 1.46 up to 1.64 were used, which was to be expected from the RI of the fibre material itself and which agrees with results of previous reported work [9]. In addition, the wavelength shift of the LPGP over the RI range from 1.46 to 1.47 was more sensitive to RI than that of LPG1; thus the wavelength shift sensitivity of the LPGP in this RI region (1.46-1.47) could be a fruitful area for further exploration, for example to develop specially-coated LPGP sensors for a range of sensing applications.

Figure 3: Comparative wavelength responses of LPGP and LPG1 over a wide range of RI change from 1.33 up to 1.46 using Cargille RI liquids

In this study, the sensors developed were tested across a RI change from 1.33 to 1.37, using NaCl solutions of 0g, 5.8g, 11.6g, 17.4g and 23.2g per 100ml deionised water. The results obtained were cross compared with the data collected over the same range utilizing Cargille RI liquids. The calculated correlation coefficients, r, to the linear fit of the data were obtained as 0.34 and 0.96 for LPG1 and LPGP respectively, and the wavelength shift response can be presented in the following equations as:

\[ \lambda = -0.0276m + 1225.1 \]  \hspace{1cm} \text{for LPG1} \hspace{1cm} (1)

and

\[ \lambda = -0.1m + 1214.3 \]  \hspace{1cm} \text{for LPGP} \hspace{1cm} (2)

where \( \lambda \) is the wavelength shift and \( m \) is the NaCl mass used (in grams per 100ml solution). The root mean square (rms) errors were obtained as \( \pm2.2g \) and \( \pm22.7g \) of NaCl for the LPGP and LPG1 respectively. The error present in the LPGP response arises mainly as a result of the low resolution of the Optical Spectrum Analyser (0.1nm). However, the error in LPG1 is mainly due to the low resolution of the sensor, which has previously been demonstrated by the low r value of the linear fit. The sensitivity demonstrated in Eq. 2 by the LPGP is higher than that of a bare and a gold coated single LPG, as reported recently in the literature [7].
The correlation coefficients, $r$, when both sensors were tested using the Cargille liquids were obtained to be 0.5469 and 0.9774 for LPG1 and LPGP respectively. The equations representing the sensor response can be described by:

$$\lambda = -15R + 1247.4 \quad \text{for LPG1}$$

(3)

and

$$\lambda = -47R + 1274.7 \quad \text{for LPGP}$$

(4)

where $R$ is the RI value. In this study, the rms errors were obtained as ±0.003 RI and ±0.02 RI for the LPGP and LPG1 respectively. As shown above, when using the NaCl concentrations or the Cargille RI liquids, the performance of the LPGP is better by a considerable margin than the LPG1 performance across the range studied.

4. Conclusion

In this work, it was shown that through the use of a LPG pair based sensor and together with interpreting the spectral information obtained, small changes in NaCl concentration could be detected. Work is on-going to continue to investigate and optimize the performance of the sensor by increasing the sensitivity of the LPG pair sensor to the phase changes measured [12, 13]. The approach being taken is to optimize the performance of the LPG pair by investigating several grating parameters and to study its operation over different regions of the spectrum. The focus of the application remains the detection of the potential for corrosion of materials such as reinforced concrete due to salt solutions and the sensor shows the potential for addressing this application in both the marine environment and for salt sprays, for example used for de-icing road surfaces in cold climates.
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