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Oxygen Sensors Based on Screen Printed Platinum and Palladium Doped Indium Oxides [†]

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Abstract: Platinum and palladium doped indium oxide sensors have been successfully fabricated by a screen printing method and tested as oxygen sensors at low temperature (150–400 °C) in a humid environment (~80–85% RH). The sensors, complying with a power law relationship, showed good differentiation at lower temperatures with highest response observed at 200 °C. Platinum had sensitivity of 2.2% per %O₂ and power law exponent $\alpha = 0.72$ vs. 0.3% per %O₂ for palladium with power law exponent $\alpha = 0.51$. Overall, the response of platinum doped indium oxide was higher than the palladium doped version.

Keywords: MOX oxygen sensor; platinum and palladium doped indium oxide; high humidity

1. Introduction

Oxygen gas sensors is one of the most common and lucrative applications of gas sensors, contributing the largest revenue share to the total of the global gas sensors market in 2013 [1]. Though oxygen can be detected using optical and electrochemical techniques (both solid-state and aqueous), the most commonly used approach is a galvanic cell, which relies on oxidation of the lead anode. [2]. Although these sensors have been highly successful, the use of lead is likely to be restricted in the near future, leading to the requirement of a lead-free replacement. While others have pursued the development of lead-free galvanic cell, we propose the use of an inorganic metal-oxide (MOX) chemiresistive sensor as a replacement. This is an attractive alternative due to its low cost (lower than lead-free alternatives), high sensitivity, compact size and easy integration with modern electronics through a simple measurement through a resistance change.

Researches on semiconducting metal oxide sensors for oxygen detection have been limited despite a large market share of oxygen gas sensors. Different materials that have been investigated for this application including Ga₂O₃ [3], SnO₂ [4], TiO₂ [5], ZnO [6], In₂O₃ [7]. Among these materials, the latter has been reported to have a high sensitivity toward oxygen at low temperatures due to its high conductivity [8].

Metal oxide gas sensors work by modulation in its conductance based on exposure to a gas or vapour. In an n-type semiconducting material, donor electrons are attracted toward oxygen, which is adsorbed on the surface of the sensing material. This causes a potential barrier that prevents electron flow thus resulting in a higher resistance at the grain boundaries. The addition of an appropriate noble metal to the semiconducting metal oxide can improve sensor performance toward targeted gas. In this work, platinum doped and palladium doped indium oxide gas sensors have been fabricated by screen printing technique and their performance was compared for differentiating oxygen concentrations.

2. Experimental

2.1. Sensor Fabrication

The sensors were produced using a thick-film screen process. Each sensor element was 2 mm × 2 mm in size and used a platinum heating element on one side and a gold electrode structure on the other. An example of the construction process used with these sensors is shown in Figure 1.

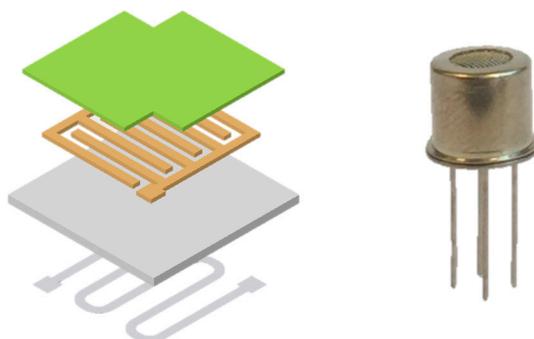


Figure 1. Sensor array top to down: sensing material, heater, alumina substrate, heater (**left**) and sensor in a TO5 fitting (**right**).

The sensing material was made of 99.9% pure -325 mesh grade indium oxide powders, activated by addition of 1% platinum and of 1% palladium (by weight). Each dopant was dispersed in the semiconducting metal oxide by wet mixing a precursor salt of the dopant in a laboratory ball mill for a couple of minutes. Cellulose-based paste sourced by McGowan Sensors was later added to the mixture and left until the solvent evaporated. Platinum and palladium doped indium oxide pastes were deposited over the interdigitated electrodes and then left to dry and unfired. At last, the sensor arrays were snapped to be individually packaged into a TO5 fitting.

2.2. Data Acquisition System

A gas handling apparatus has been constructed to carry out gas testing in School of Engineering, University of Warwick. The system can supply a predefined concentration of oxygen by diluting 99.999% N₂ (Leman Instrument, France) with zero air (20% O₂). The tests were carried out by varying flow rates of the individual gas with the total flow rate kept at 300 mL/min using a computer programmed in LabVIEW (National Instruments 2016). Each of the gas lines was passed through a mass flow calibrator and the output gases were then combined into a single stream prior to entering gas inlet of the chamber where the sensors were housed. A water bubbler connected between gas mixture and gas chamber inlet provides 80–85% relative humidity. The sensors devices were mounted in a gas-tight chamber connected to AS-330 Sensor Management System (Atmospheric Sensor Ltd., Sandy, UK) with a 9 pin D-type connector. The Sensor Management System (SMS) can work with up to 8 gas sensors, allowing different range of operating temperature, test period, and individual sensor heater resistance which can be set as parameters. The output data from the software include sensors resistance, impedance, temperature, and current.

3. Results and Discussion

3.1. Material Characterisation

Figure 2 illustrates the SEM microstructure of Pt-In₂O₃ and Pd-In₂O₃. Both Pd and Pt dispersed indium oxide exhibited porous structures which are likely to facilitate oxygen adsorption.

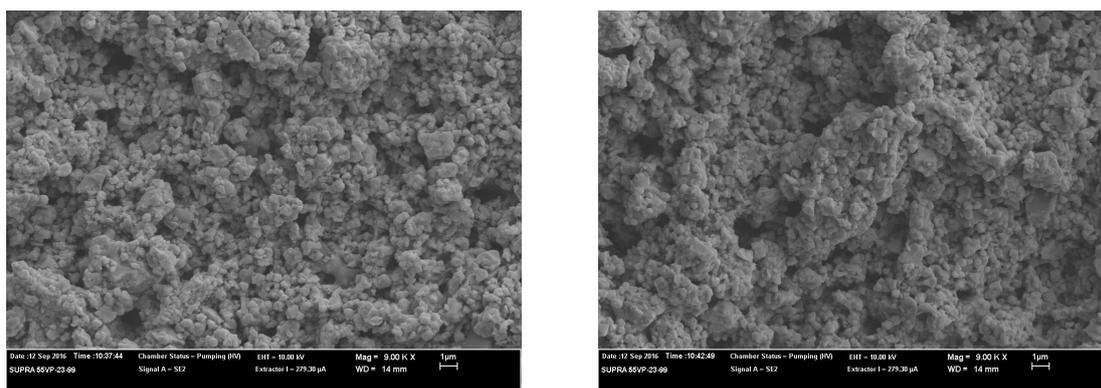


Figure 2. SEM images of Pd-In₂O₃ (left) and Pt-In₂O₃ (right).

3.2. Gas Testing

Sensor measurements were carried out from 150 °C to 400 °C in high humidity environment (RH 80–85%). Base resistance of Pt-indium oxide (<1 kOhm) was lower than Pd-indium (up to 6.5 kOhm) oxide for the whole temperature range, as shown in Figure 3. The resistance at 20% O₂ of Pt- and Pd-indium oxide were found to decrease from 150 °C to 200 °C which may be due to thermal activation of electrons from valence band to the conduction band [9]. Pt-In₂O₃ sensor had an increased resistance at 150–350 °C as oxygen molecules undergo dissociation and adsorbed as ions attracting more electrons from the metal oxide. At 400 °C, the resistance decreased presumably due to adsorbed molecules overcoming an energy barrier to desorb from the metal oxide. Pd-In₂O₃ also showed an increased resistance at 250 °C, but it further decreased to 400 °C. This might suggest palladium was able to overcome the energy barriers at lower temperature or Pt- and Pd-indium oxide had different sensing mechanism.

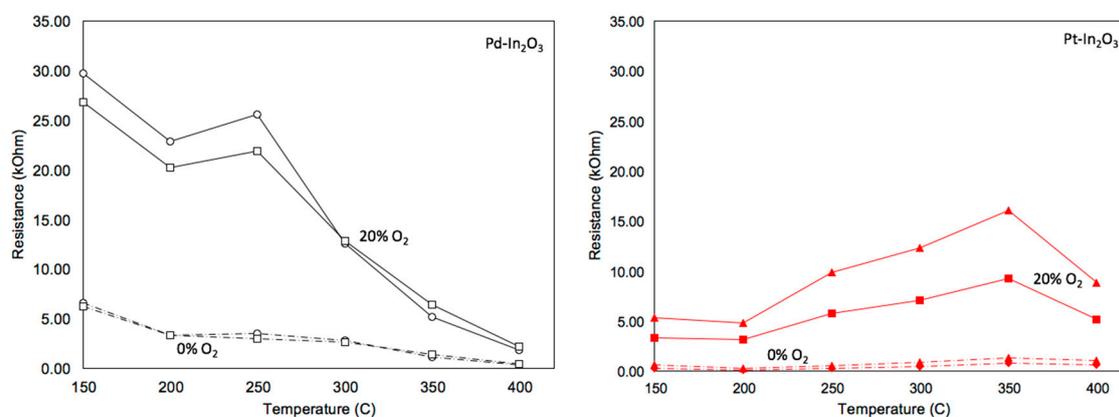


Figure 3. Average resistance values of Pd-In₂O₃ (left) and Pt-In₂O₃ (right).

Figure 4 illustrates dynamic response of platinum and palladium indium sensors for comparison. Both sensors showed good sensitivity from 150 °C with the maximum response obtained at 200 °C for both Pt-In₂O₃ and Pd-In₂O₃. Sensor response was expressed as $(R_g - R_0)/R_0$ where R_g represents resistance of O₂ at certain concentration and R_0 is of N₂ resistance. Platinum showed superior response towards oxygen compared to palladium at almost 8× higher $(R_g - R_0)/R_0 = 44$ or 2.2 per %O₂ vs. $(R_g - R_0)/R_0 = 6$ or 0.3 per %O₂.

Both type of sensors complied with traditional power law relationship, with Pt-In₂O₃ showing good response with alpha value between 0.65 and 0.72 and Pd-In₂O₃ between 0.46 and 0.51. Sensitivity of sensors upon gas exposure at different oxygen, illustrated in Figure 4, showed platinum indium oxide exhibiting higher sensitivity than palladium indium oxide in the whole range of temperature investigated.

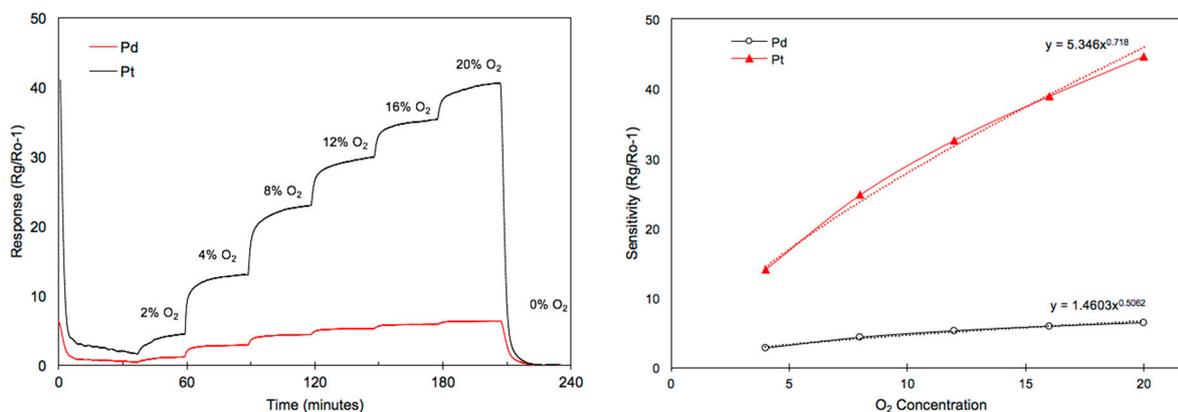


Figure 4. Dynamic response (**left**) and sensitivity (**right**) of indium oxide based sensors to different O₂ concentrations at 200 °C.

3. Conclusions

Platinum and palladium indium oxide were investigated for the detection of oxygen in a humid environment. The sensors materials were deposited onto alumina substrates via screen printing. Results showed our sensors exhibited good sensitivity toward oxygen, following traditional power law over 0–20% concentration range. In comparison with Pd-In₂O₃, Pt-In₂O₃ showed a much higher sensitivity and better response (2.2% per %O₂ vs. 0.3 per %O₂ for Pd-In₂O₃), making it better candidate as an alternative to existing Pb-based sensors. However, the effect of cross-sensitivity to other gases still requires investigation before a judgement can be made on the full potential of the Pb-In₂O₃ system.

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Conflicts of Interest: The authors declare no conflict of interest.

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