



Short communication

Electrical characterization of a mixed potential propylene sensor



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ABSTRACT

In this article, electrical characterization of a 'La_{0.8}Sr_{0.2}CrO₃/YSZ/Pt' non-Nernstian propylene gas sensor is reported. The effect of the concentration of the test gas (25–200 ppm) on the sensor response was studied using impedance spectroscopy and current–voltage curves. For a fixed operating temperature of 510° C, the interfacial resistance was seen to decrease with increase in the analyte concentration. A 48% reduction in interfacial resistance has been observed when switched from air to 200 ppm of propylene. I–V studies show a non-linear relationship. The slope of the curves around zero current matches the resistances measured by ac impedance. The controlled interface sensor design facilitated impedancetric and potentiometric sensing schemes.

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1. Introduction

The number of automobiles has been drastically increasing over time, which in turn, has led to a significant increase in the gas phase pollutants exhausted into the atmosphere. Among the various pollutants such as nitrogen oxides (NO, NO₂), carbon monoxide (CO) and hydrocarbons (HCs), the non-methane HCs indirectly expedite the generation of a photochemical smog (leading to greenhouse effects) [1,2]. In order to reduce the HCs exhausted from automobiles, the three-way catalyst (TWC) system is in place [3]. In this system, the HCs can be oxidized to environmentally benign CO₂ and H₂O. To control the efficiency of the catalysis operation and detect the concentration of the unreacted HCs, sensitive and selective HC sensors need to be placed downstream of the TWC. So far, there have been numerous reports on HC sensors with different sensing modalities [4–9]. The most examined ones are solid–electrolyte type [10,11], and semiconductor-based gas sensors [12,13]. Among them, the mixed-potential-type Ytria-stabilized zirconia (YSZ)-based sensors have been one of potential candidates due to the simplicity of fabrication and operation as well as the ability to detect different gases sensitively and selectively at high temperature [14].

Mixed potential sensors are a class of electrochemical devices, which develop a non-Nernstian electromotive force (e.m.f) due to the difference in the kinetics of the redox reactions at each electrode/electrolyte interface upon exposure to various analytes

[15]. These sensors rely on the fact that two dissimilar electrodes along with an oxygen-ion conducting electrolyte exhibit different non-equilibrium potentials in the presence of a reducing gas and oxygen. The mixed potential based sensing mechanism facilitates sensor implementation with low power consumption, miniaturization, and a direct voltage read-out circumventing the need for any additional conditioning circuitry. In this electrochemical modality, the mixed potential strongly depends on the catalytic and electrocatalytic properties near the three phase interface (electrode/electrolyte/gas). The sensors need to be characterized in order to achieve the desired performance specifications. Electrical characterization of the sensors is vital to the understanding of the processes that might occur at the interface governing the sensor response.

Impedance spectroscopy (IS) is the study of electrical impedance of a system or material as a function of frequency. It has been routinely used as an investigative and diagnostic probe in a wide variety of applications including sensing [16–19]. A review article by Pejic et al. [20] summarizes over 35 years (1970–2006) of research investigation on the use of IS in electrochemical sensor optimization. According to the reviewed literature, IS has been used to provide information on various fundamental processes (i.e., adsorption/film formation, rate of charge transfer, ion exchange, diffusion, etc.) that occur at the electrode–electrolyte interface. On the other hand, the current–voltage curves can provide an insight on the linearity of the electrochemical processes that occurs at the interface along with charge–transfer resistance values.

In this article, electrical characterization of a 'La_{0.8}Sr_{0.2}CrO₃/YSZ/Pt' mixed potential based propylene gas sensor is reported. The electrode selection for sensing propylene

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was based on an earlier premise [21,22] that $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ was suited to measure non-methane hydrocarbons in the temperature range 400–650 °C in lean burn conditions. The effect of the concentration of the test gas (0–200 ppm) on the sensor response is studied using impedance spectroscopy and current–voltage curves.

2. Experimental

The $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ powder was obtained from Praxair® and was pressed into a pellet and sintered at 1650 °C for 10 h in order to form a dense ceramic. The ceramic pellet was cut into smaller pellets with dimensions of approximately 0.2 cm × 0.2 cm × 0.2 cm. The pellet was buried in YSZ tape-cast film and pressed uniaxially at 1500 lbs in either a 1/2" diameter or 3/4" diameter die for 5 min. The excess YSZ was removed from the surface of the chromate pellet using a razor blade. Once a clear electrode/electrolyte interface was exposed, the pellet was sintered at 1200 °C for 10 h. A 0.004" Pt wire was buried onto the surface of the chromite electrode and co-sintered. The other electrode was a Pt (0.01") wire buried into the YSZ electrolyte. The sensor was attached to Pt (0.01") leads and placed onto a platform made from machinable ceramic (MACOR). The fabricated sensor was mounted on an alumina rod with Pt leads and placed in a quartz tube, which was then heated in a tube furnace to the desired operating temperature. An operating temperature of 510 °C was chosen for this experiment based on previous investigation [23]. Propylene was used as the analyte and synthetic air was used as the base gas. The total flow rate (base + test) was set at 200 sccm. Further, the flow rate of the test gas was adjusted so as to give the desired concentration in the test fixture. The partial pressure of O_2 was maintained at 21%. After completing the experimental set-up, the propylene concentration was varied from 0 to 200 ppm. These experiments were performed on sensors fabricated with YSZ sintered at 1200 °C. The sensor response was monitored in each case. Keithley 2400 source meter unit was used to measure the sensor output (with the Pt electrode connected to its positive terminal). The sensor response is defined as the difference in e.m.f generated upon exposure to the test and base gas respectively. Two-electrode AC impedance measurement was performed using a Solartron SI 1260 impedance/gain phase analyzer with a frequency sweep from 13 MHz down to 10 mHz and a perturbation of 10 mV. Using Solartron 1287 Potentiostat/Galvanostat, the I–V curves were recorded. The voltage was swept from –0.25 V to +0.25 V at the rate of 0.3 mV/s. Electrical equivalent circuit parameters describing the bulk and interfacial reactions were extracted from the impedance spectrum to get an insight on the electrochemical processes as a function of propylene concentration.

Propylene is the analyte of interest as it is typically used as a simulant to test the TWC system [24,25]. The concentration of the propylene in pre-TWC stoichiometric engine exhaust ($\lambda = 0.9$) is 0.045 vol.% and post-TWC is 0.0001 vol.%. Propane or propylene at 510 °C gets completely electrochemically oxidized irrespective of the complex pathways for oxidation. Hence, both propane and propylene would be good analytes to explore the nature of mixed potential and electrical characterization of the sensor for automotive emissions control applications.

3. Results and discussion

In an earlier study [26], porous YSZ electrolyte was found to play a significant role in the heterogeneous catalysis of propylene and in general, hydrocarbons.

The heterogeneous catalysis, which takes place at elevated temperature in presence of excess O_2 , can have a large effect on the observed response of the mixed potential sensor using YSZ as the

electrolyte. The rough YSZ surface is seen to greatly reduce the amount of C_3H_6 for electrochemical oxidation at the electrode/YSZ interface. The heterogeneous catalysis effect diminishes the sensor response (in terms of sensitivity) and constricts the impedance curve. Since the sensor described in this article is made of YSZ, the presented results include the heterogeneous catalysis effect and are not separated out. Through the use of inert coatings on YSZ, the amount of heterogeneous catalysis can be reduced so that subsequent studies can now focus on the selectivity properties of other potential electrode candidates. If heterogeneous catalysis were to be minimized, then the sensitivity of the sensor presented would have increased two fold. The effect of propylene oxidation on Pt and Perovskite electrodes are discussed in detail in earlier studies [27].

In mixed potential sensors, the presence of different analytes and at different concentrations is expected to alter the impedance at low frequencies in a repeatable fashion. First, gases diffuse to the electrode surfaces, where they adsorb, dissociate, and diffuse along the surface to the electrode–electrolyte interface, followed by charge transfer (redox) reactions. Then ion transport through the electrolyte occurs with charge transfer across grain boundaries. At various frequencies, some of the processes may contribute to the impedance response, depending on the physical characteristics of the electrochemical cell and analyte species.

In an impedance spectrum obtained from an electrochemical device, the contributions of the bulk electrolyte and the electrode/electrolyte interface are identified by the frequency dispersions. In general, the low frequency region represents the electrode polarization/charge transfer phenomenon while the high frequency component represents the bulk conductivity of the sample. It is to be noted that the bulk conductivity of the sample is an additive effect of the ionic conductivity of the electrolyte, electronic conductivity of the electrodes, and electronic conductivity of the leads. As the ionic conduction in the electrolyte forms a major representation of the high frequency portion of the Nyquist plot, in further sections, the bulk conductivity of the sample will be approximated to the ionic conductivity of the electrolyte.

Fig. 1 illustrates the AC impedance response of the sensor for various propylene concentrations at a fixed operating temperature of 510 °C upon exposure to propylene. The various shapes (circle, square, diamond, and cross) represent the data points and the dotted line represents the fit. Two parallel branches of R (resistance) and Q (constant phase element, CPE) circuit connected in series representing the electrolyte (B stands for bulk) and electrode/electrolyte/gas interface (I stands for interface) was used to fit the impedance response. The CPE was used to account for the non-ideal behavior of the electrolyte capacitance and the interfacial capacitance. The fitting circuit (shown as an inset in Fig. 1) reported earlier [23] was used in the investigation. The circuit uses 'EQUIV-CRT' program developed by Boukamp [28] to fit the impedance data.

The semi-circles at the high frequency region (starting from 13 MHz and ending at 2.5 KHz) that represents the resistance to oxygen conduction in YSZ seems to be unaffected by change in propylene concentration. However, the large arc (starting from 2.5 KHz and ending at 10 mHz) at the low frequency region has been considerably pulled down toward the real Z-axis after 72.1 mHz with increasing propylene concentration, from 0 (air) to 200 ppm. The impedance spectrum seems to indicate a change in interfacial impedance with varying concentration of propylene. Table 1 lists the electrical equivalent circuit parameter values based on fitting the impedance data (Fig. 1). Resistance element R_B provides information regarding oxygen transport in the electrolyte, while R_I is indicative of charge transfer process at the electrode–electrolyte interface. The CPEs, a measure of the capacitance, arise due to build-up of O^{2-} ions. n_B and n_I are the exponents associated with the

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