

Development of Methanol Sensing Devices with Cobalt-doped SrFeO_{2.5+x} Thin-films Perovskites Prepared by Pulsed Laser Deposition (PLD): Towards the Fabrication of Methanol Sensors for Direct Methanol Fuel Cell Applications

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Abstract: Thin films of gas sensitive materials based on the SrFeO_{2.5+x} non-stoichiometric perovskite family were deposited onto an interdigitated gold electrode construction device by room temperature pulsed excimer laser deposition (RT-PLD). Two films sensors based on the SrFe_{1-y}Co_yO_{2.5+x} oxides perovskite family, with y = 0.75 and 0.5 respectively, have been presented. Their ability to very quickly respond to the presence of low concentrations of methanol makes them attractive for construction of methanol sensing devices, as gases monitoring sensors for either environmental applications, or as an automated feedback sensor for concentration measurement and control in a micro direct methanol fuel cell (μ -DMFC) power supply. In this paper, we report unpublished hitherto results first presented as poster during an *Electrochemical Society* Symposium session held at Queen University, Kingston, Ontario, Canada.

Keywords: Fuel Cell; Methanol; Perovskite; Pulsed Laser Deposition; Sensor; Thin Film

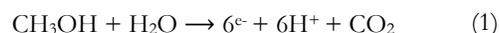
1. Introduction

1.1. Statement and Motivation of the Necessity of Gas Sensors

Among the increasing number of driving forces leading to the need for monitoring gases can be improvements in indoor air quality, safety, spill detection, automotive, food, pharmaceutical, petrochemical, etc., where sensor technology is ever more important for determining real-time physical parameters and chemical concentration of complex analytes. Gas sensors are also needed in process control or efficiency, productivity, safety, and also addressing regulatory requirements. Of particular relevance in these areas is the fabrication of miniature devices by integration of chemical sensor materials with platforms, whereby the functionality of the created device is significantly improved. The approach is to provide a sensor which is compact, inexpensive, low power, low maintenance, and yet with a capability of real time response with analyses of multicomponents in a given environment. Such a device can be conveniently deployed in multipoint locations to satisfy a range of monitoring requirements over a large area.

One of the most interesting applications of gas sensing is the fuel monitoring and control in direct methanol fuel cells (DMFC) power supply. DMFC is a renewable energy source which works at near room temperature, and allows for easier liquid fuel storage, which makes it a potential power supply candidate. Unlike a hydrogen polymer electrolyte fuel cell (H₂-PEMFC), the DMFC does not require ancillary components such as a separate humidifier, fuel processor, or cooling system. At the

beginning of this new millennium, several organizations including Motorola (Bostaph *et al.*, 2001), Jet Propulsion Laboratory (Narayanan *et al.*, 2001), the University of Minnesota (Kelly *et al.*, 2000) and the National Research Council of Canada (NRC) have undertaken aggressively research programs aimed to develop micro direct methanol fuel cells for MEMS applications. Within the methanol fuel cell, electricity is produced by a simple anodic methanol oxidation reaction, shown as:



In the above reaction, the production of the CO₂ bubbles forces the flow upward to the exit of the anode plate. As this CO₂ is not returned back in the feed system, the concentration of methanol, the fuel, is continuously decreased. Therefore, pure methanol must be added to the solution loop to maintain the required concentration. Thus, the concentration of methanol in the fuel circulation loop of any DMFC system is an important operating parameter, because it determines the electrical performance and efficiency of the system. The methanol concentration in the circulating fuel stream can be measured continuously and maintained at a predefined level with a suitable sensor. A calculated molarity value of methanol is used as the input to a decision making loop that control the methanol feed pump. Various methods of sensing methanol concentration have been proposed over the past decade (Narayanan *et al.*, 1998) for robust systems but at our knowledge, nothing has yet been done concerning micro-DMFC constructions.

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The results presented in this paper are the findings of a preliminary study performed in the framework of a vast research within multidisciplinary program undertaken at the National Research Council of Canada (NRC). Thus, the extent of work reported here represents only a small part of an ongoing investigation on certain complex systems that include the methanol/water mixture for use in a Direct Methanol Fuel Cell (DMFC). To be more precise, the present research work addresses the development of thin-films of complex metal oxides of the nonstoichiometric perovskite family for methanol sensing, as a preliminary step for further application in the fabrication of cantilever-based methanol sensors for a DMFC power supply integrated in complex MEMS devices. One of the strategic economic applications behind the above research program is the fabrication of a MEMS device that can be used as a radio-frequency (RF) remote control system for pipelines installations monitoring or for various advanced defense applications.

1.2. Background and Structure of Perovskite $\text{SrFeO}_{2.5+x}$

Perovskite is a calcium titanium oxide mineral species composed of calcium titanate, with the chemical formula of CaTiO_3 . The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist, L. A. Perovski (1792–1856). Since then, perovskite lends its name to the class of compounds which have the same type of crystal structure as CaTiO_3 (ABO_3) known as the perovskite structure (Hench and West, 1990). The perovskite crystal structure was first published in 1945 from X-ray diffraction data on barium titanate by the Irish crystallographer Helen Dick McGaw (1907–2002).

It is a ternary compound of the formula ABO_3 for which A and B cations differ in size. It is considered to be an FCC-derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. There is only oxygen being B cation's nearest neighbor. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes (Goldschmidt, 1926). The unit cell of a perovskite cubic structure is shown in Figure 1. Oxides with perovskite and related structures with mixed electronic ionic conductivity are of interest as electrode materials, oxidation catalysts, ion-transport membrane materials and in thin film sensors. For the latter application, the group of Nanostructured Materials of the Institute for Chemical Process and Environmental Technology (ICPET)/NRC, has extensively studied thin films of the non-stoichiometric perovskite $\text{SrFeO}_{2.5+x}$ grown onto sapphire substrates by the pulsed excimer laser deposition (PLD) technique (Post *et al.*, 1999a; Post *et al.*, 1999b; Tunney and Post, 2000; Grudin *et al.*, 2002).

The structure, electrical conductivity and phase behavior of bulk samples of $\text{SrFeO}_{2.5+x}$ have been

examined by several other groups (Tofield *et al.*, 1975; Takeda *et al.*, 1986; Mizusaki *et al.*, 1992; Kozhevnikov *et al.*, 2001). At high oxygen partial pressures, $\text{SrFeO}_{2.5+x}$ adopts the perovskite structure and transforms to the vacancy-ordered brown millerite structure when the oxygen partial pressure is lowered. At lower temperatures, other intermediate vacancy-ordered structures are known.

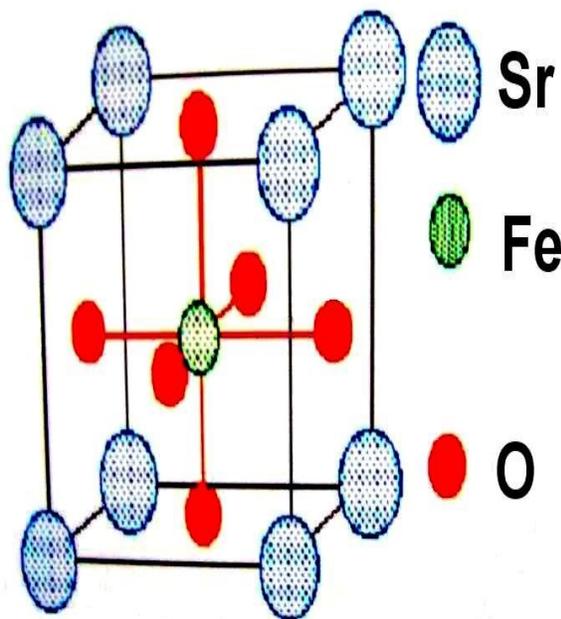


Figure 1. General structure of the SFO perovskite.

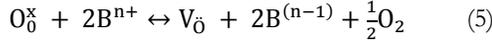
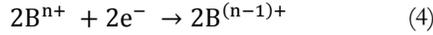
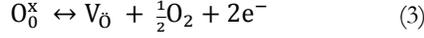
The chemistry of the strontium-iron-based $\text{SrFeO}_{2.5+x}$ perovskite materials predicts a catalytically induced reduction of the SFO when in contact with a gas phase of a reducing analyte, e.g. methanol. It has been also observed that the perovskite structure $\text{ABO}_{2.5+x}$ is tolerant to elemental substitution in both the A and B sites. For this research, the parent $\text{SrFeO}_{2.5+x}$ perovskite compounds and their thin films have been chemically and morphologically modified to focus on the cobalt substituted series of the $\text{SrFe}_{1-y}\text{Co}_y\text{O}_{2.5+x}$, abbreviated as SFCO's family, for $0 < y < 1$ (Post *et al.*, 1999a). Such a cobalt substitution confers upon these compounds a higher degree of mixed ionic/electronic conductivity (Grudin *et al.*, 2002) than is present in $\text{SrFeO}_{2.5+x}$. These attributes provide a more tunable sensor response with respect to the chemical-sensor orthogonality. Additionally, at ambient temperature, SFO films were found to have sheet resistance greater than $220 \text{ M}\Omega/\text{sq}$, while the cobalt-substituted films were found to have a measurable electrical resistance and a sheet resistance in the range of $30\text{--}40 \text{ M}\Omega/\text{sq}$.

1.3. Theoretical Background and Gas Sensing Requirements

The gas sensing activity of thin film sensors works by thermal activation of charge carriers:

$$\sigma = A\sigma_0 e^{-\left[\frac{E_c - E_t}{kT}\right]} \quad (2)$$

where σ is the minimum conductivity after the adsorption of a reducing gas; σ_0 is the conductivity in a steady gas flow; A is a constant; E_c is the energy of the conduction band, and E_t is the energy of the surface state. The oxygen defect equilibrium:



Equation 3 is the formation of an oxygen vacancy with loss of two electrons. Equation 4 is the reduction of the metal from B^{n+} to $B^{(n-1)+}$. Under a rich-oxygen environment, the equilibrium in equation 5 is moved to left, which is responsible for the formation of electron holes, which provide more active sites.

In the case of the MeOH/H₂O system, the MeOH behavior (vapor pressure VP vs molar fraction of MeOH in water) in a DMFC is better described by the Antoine equation as:

$$\log_{10}P^* = A - \frac{B}{T + C} \quad (6)$$

where P^* is the vapor pressure in mm Hg and T is the heat temperature in degree Celsius. Figure 2 shows the variation of the vapor pressure of a MeOH/water system at different concentrations of methanol. As methanol has the properties of a reducing gas, the sensitivity (S) of p -type SFOC semiconductor thin films gas sensors would be determined using the following equation:

$$S = \frac{R_{\text{gas}} - R_{\text{air}}}{R_{\text{air}}} \quad (7)$$

where R_{air} and R_{gas} are the electrical resistance in air and in an atmosphere containing a constant gas concentration to be monitored, respectively. For such a system, the following mechanism for methanol sensing is proposed:



When the composition of the air surrounding the device is altered by the presence of a reactive gas, i.e. methanol, an interaction occurs which results in a change in the availability of electronic conductors. Then the impedance changes as result of chemically induced change to the sensor material. This resistance is then used as a measure of the concentration of the trace gas. In order to obtain sufficiently fast kinetics for film–gas chemistry and to provide a rapid sensor response, the thin film must be heated to approximately 500 °C or higher (Post *et al.*, 1999b). The electrical resistance of the film is then measured before, during and after exposure to the analyte gas stream to yield a form of sensor transduction signal which can then be simply monitored by an on-board circuitry for analysis and processing (Tunney and Post, 2000).

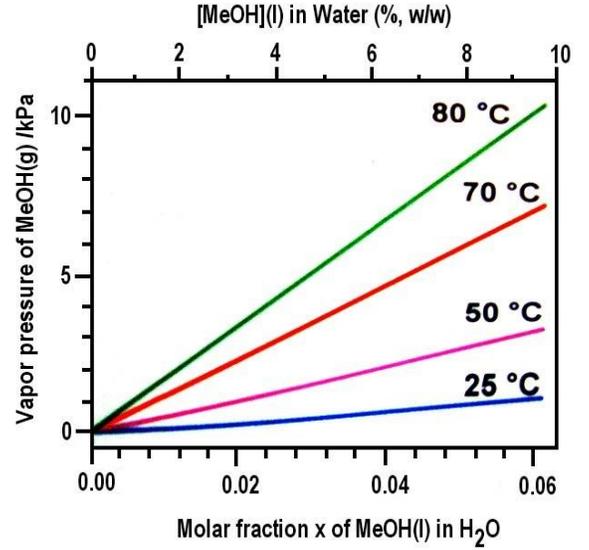


Figure 2. Variation of the vapor pressure of methanol in a MeOH/H₂O system for different concentrations and different temperatures.

Due to the p -type conductivity of the sensing film, certain interesting characteristics are obtained. For example, the resistance of the film increases in a reducing environment. This extends the measurement range of these films to concentrations beyond those accessible to commonly available conventional SnO₂ sensors, which are n -type semiconductors, and approach an $R = 0\Omega$ value at higher gas exposure concentrations.

1.4. Background on Films Deposition and Characterization

SrFe_{1-y}Co_yO_{2.5+x} thin films of good quality are obtained by pulsed laser deposition (PLD) and characterized by x-ray diffraction (XRD). Inductively coupled plasma-Auger electron spectroscopy (ICP–AES) has shown them to be single phase with a well defined chemical composition (Grudin *et al.*, 2002), thus confirming congruent transfer during PLD. It was also determined that for the SFCO family, films could be successfully deposited by PLD onto substrates over a range of temperatures from room temperature (then denoted as SFCO-RT) to 300 °C, with subsequent annealing during a preconditioning step to optimize sensor functionality (in contrast to the parent SrFeO_{2.5+x}). The p -type semiconducting films obtained by such a procedure are found to adhere onto the substrate they are deposited, with a uniform thickness of approximately 200 nm. The avoidance of higher temperatures (i.e., $T > 300$ °C) during PLD is advantageous for minimizing the thermal stress that may be experienced by the host electrode substrate, then preserving its integrity. Investigations of the reduction–oxidation properties of the SrFe_{1-y}Co_yO_{2.5+x} family (Post *et al.*, 1999a; Grudin *et al.*, 2002) have determined that the optimum composition for enhanced sensing functionality is with $y = 0.75$.

2. Materials and Methods

2.1. Synthesis and Characterization of Materials

The $\text{SrFe}_{1-y}\text{Co}_y\text{O}_{2.5+x}$ ($y = 0.50$ and $y = 0.75$) targets were prepared by conventional ceramic preparation techniques. SrCO_3 , Fe_2O_3 and Co_3O_4 powders (> 99.9% pure on a metal basis) were mixed and ground together in the required quantity, followed by heat treatment at 1100 °C under oxygen atmosphere. The sample was ground up again and characterized by XRD. Once the single-phase product was obtained in powdered form, the powder was pelletized and sintered at 1150 °C in oxygen. After XRD analysis confirmed the pellet to be single phase, the pellet was used as the target material for the deposition of either $\text{SrFe}_{0.50}\text{Co}_{0.50}\text{O}_{2.5+x}$ or $\text{SrFe}_{0.25}\text{Co}_{0.75}\text{O}_{2.5+x}$ films by PLD.

2.2. Material Deposition and Device Fabrication

$\text{SrFe}_{0.50}\text{Co}_{0.50}\text{O}_{2.5+x}$ or $\text{SrFe}_{0.25}\text{Co}_{0.75}\text{O}_{2.5+x}$ films were deposited by the PLD technique on interdigitated gold electrode substrates using a Lambda-Physik LPX305i excimer laser operating with Kr/F at 248 nm. All depositions were carried out under a background oxygen pressure of 100 m Torr. The films, typically 200 nm thick, were fabricated by ablating the $\text{SrFe}_{1-y}\text{Co}_y\text{O}_{2.5+x}$ target with the laser operating at 8 Hz and at an energy fluence of 1.5 J cm⁻². The average deposition rate was 10 nm minute⁻¹. For the device construction, we have used a seven-pin sensor platform provided by the Armstrong Monitoring Corporation (Figure 3).

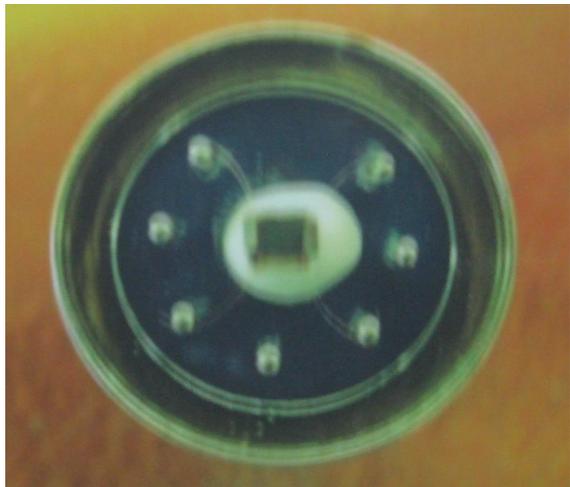


Figure 3. A seven-pin sensor platform with a wire-bonded thin film.

An interdigitated gold electrode substrate (Figure 4) onto which we have deposited the sensor film material by PLD was then wire-bonded and mounted on the above seven-pin sensor platform. This platform was connected to a readout circuit with two pins connected to a heater circuit to warm the film sensor to an “active” temperature and a measurement circuit in which the impedance of the semiconductor material is measured and displayed.

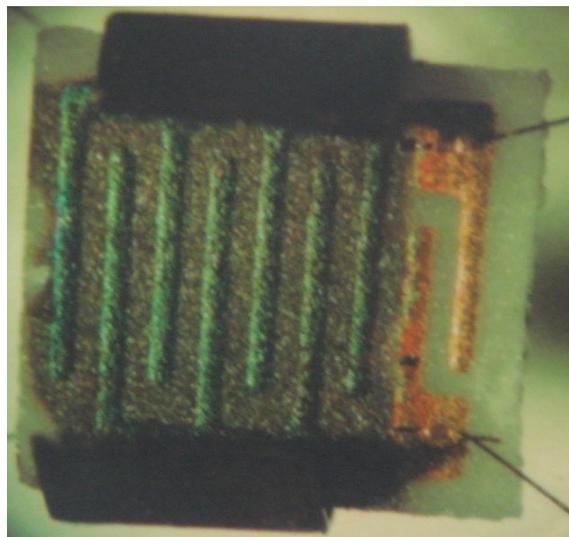


Figure 4. An interdigitated gold electrode thin film substrate with a SFOC film.

The gas-sensing device was then suspended in a reactive chamber made of a four-liter Pyrex glass container. A plastic drain plug mounted and sealed on the top of the Pyrex container was equipped with a series of ports that served to introduce the sensor in the Pyrex container, to perform an injection of methanol into the reactive chamber, to flush out the methanol after reaction and sometimes to introduce oxygen from ambient air by simple opening.

3. Results and Discussion

In this study, the methanol sensing of two SFOC semiconductors *p*-type materials has been investigated. Gas sensor functionality was determined by in-situ measurement of the electrical conductivity of the sensors in a custom fabricated chamber made of a Pyrex container and a gas injection system.

Even if some literature seems to favor a SFCO material with a doping in Fe/Co in the proportions of 0.25/0.75, we have recognized that the difference in sensitivity observed between the 0.50/0.50 and the 0.25/0.75 systems was not considerable (Figure 5).

Both compositions, especially the 0.50/0.50 system, have a good stability upon heating and present a very stable region of temperature in which the sensor was thermodynamically stable, i.e. the region in which the resistance does not fluctuate with time (Figure 6). An important shift of the resistance is also observed after multiple and repetitive exposures (ageing) of the sensor to methanol (Figure 7). Ageing a film sensor seems to enhance its sensitivity for MeOH.

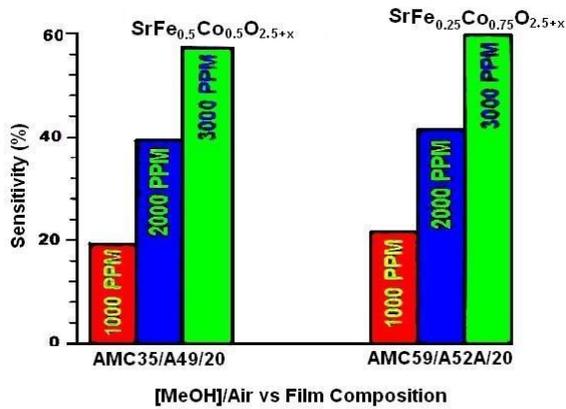


Figure 5. Effect of composition and doping ratio of Fe/Co into the SFO thin-film sensors exposed to different concentrations of MeOH/air mixture.

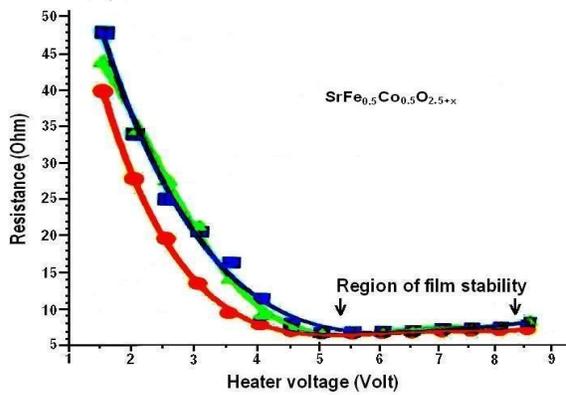


Figure 6. Variation of the electrical resistance of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin-film sensor in air at different heat treatments.

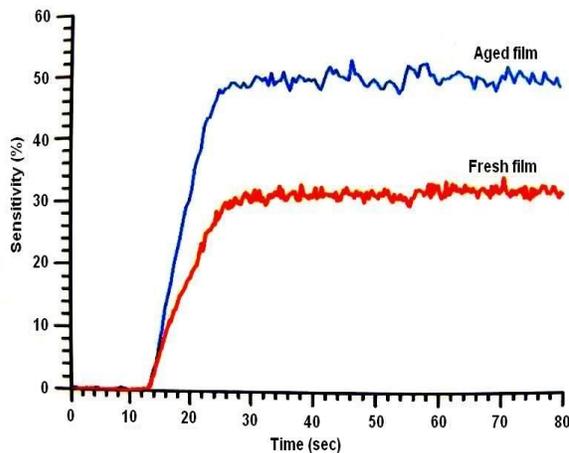


Figure 7. Sensitivity of a fresh and a previously aged $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin-film sensor exposed to 700 ppm of methanol/air.

Another important observation was that the starting resistance point was always reproduced for any single test scan and the recovery time, i.e. the necessary time required before the sensor may be re-used, was roughly

10 to 20 seconds (Figure 8). As expected, high concentrations of MeOH led to longer recovery times because of possible poisoning due to the saturation of the sensor active surface by the reducing gas. Moreover, all the film sensors tested have shown a very remarkable ability to reproduce signal readings when they were consecutively exposed to the same concentration of methanol (Figure 8). There was a well-defined linear relationship between the sensitivity and concentration of methanol (Figure 9). This is an important observation that makes these materials good candidates for use in methanol sensor devices.

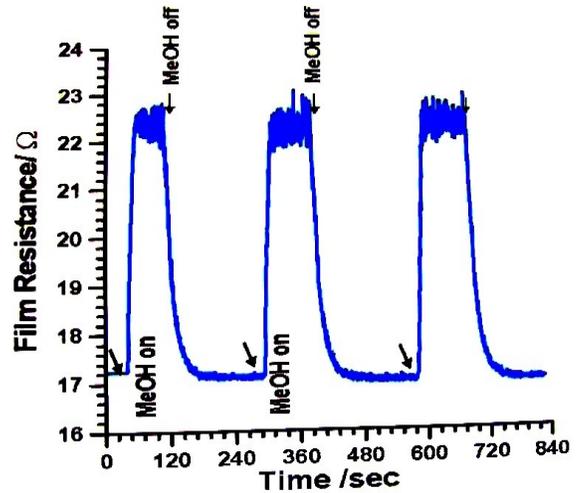


Figure 8. Typical response and recovery transients of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin-film sensor quickly exposed to 700 ppm of methanol in air.

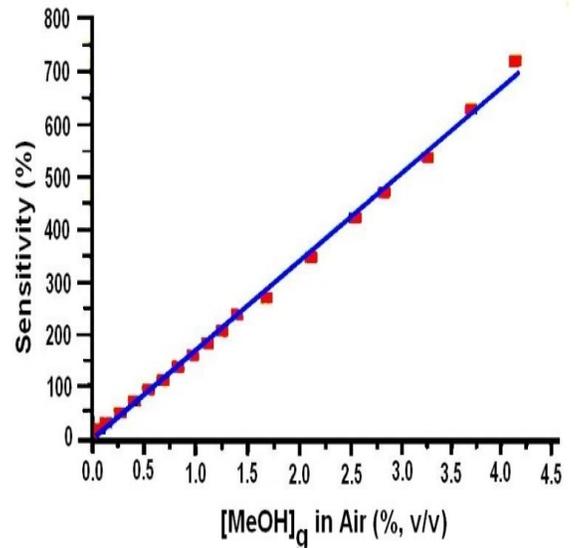


Figure 9. Maximum sensitivity of a $SrFe_{0.5}Co_{0.5}O_{2.5+x}$ thin-film sensor exposed to different concentrations of methanol in air.

Finally, the speed of response, i.e. the time required for a film sensor to reach a certain fraction of its real

maximum sensitivity, was also very good as displayed on Figure 10 for the $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.5+x}$ system. The results showed rapid response and high sensitivity; the gap of resistance covered predicts good sensitivity even down to concentrations in the low ppm range.

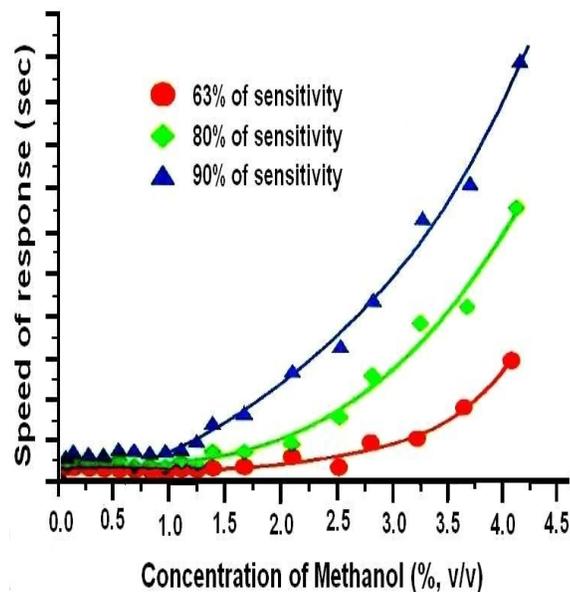


Figure 10. Typical speed response of a $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{2.5+x}$ thin-film sensor exposed to different concentrations of methanol in air for selected sensitivities.

4. Conclusion

To summarize, thin-films of gas sensitive materials based on the $\text{SrFeO}_{2.5+x}$ nonstoichiometric perovskite family were deposited by RT pulsed excimer laser deposition onto an interdigitated gold electrode substrate, wire-bonded and mounted on a seven-pin sensor platform. Two films sensors based on the $\text{SrFe}_{1-y}\text{Co}_y\text{O}_{2.5+x}$ oxides perovskite family, with $y = 0.25$ and 0.5 , have been considered. Their ability to very quickly respond to the presence of low concentrations of methanol makes them attractive for the construction of methanol sensing devices, such as gas monitoring. This research work was a preliminary study for complex systems such as the methanol/water mixture. Further studies are underway and are aimed to the development and optimization of a micro methanol sensor for a micro direct methanol fuel cell (μ -DMFC) powered device.

5. Acknowledgment

The authors would like to gratefully acknowledge of X. Du for her invaluable help by performing the films deposition by PLD. This work was partially supported by NSERC, the NRC/NSERC Collaborative Research Program and the NSERC/AMC (Armstrong Monitoring Corporation) partnership program.

6. References

- Bostaph, J., Koripella, R., Fisher, A., Zindel, D., Hallmark, J. and Neutzler, J. 2001. Microfluidic fuel delivery for 100 m W DMFC. *In: Proceedings of the Symposium on Direct Methanol Fuel Cells. The 199th Electrochemical Society Proceedings Series*, Princeton, NJ, USA.
- Goldschmidt, V.M. 1926. *Skrifter Norske Videnskaps-Akad, Oslo, I: Mat. Nature K12*: 8.
- Grudin, O., Marinescu, R., Landsberger, L.M., Kahrizi M., Frolov, G., Cheeke, J.D.N., Chehab, S., Post M.L., Tunney, J.J., Du, X., Yang, D. and Segall, D. 2002. High-temperature gas sensor using perovskite thin films on a suspended microheater. *Journal of Vacuum Science and Technology* 20(3): 1100-1104.
- Hench, L.L. and West, L.K. 1990. *Principles of Electronic Ceramics*. John Wiley and Sons, Inc., USA.
- Kelly, S.C, Deluga, G.A. and Smyrl, W. 2000. A miniature methanol polymer electrolyte fuel cell. *Electrochemical and Solid State Letters* 3(9): 407-409.
- Kozhevnikov, V.L, Leonidov, I.A, Patrakeev, M.V., Mitberg, E.B. and Poepelmeier, K.R. 2001. Electrical Properties of the Ferrite SrFeO_y at High Temperatures. *Journal of Solid State Chemistry* 158 (2): 119-364.
- Mizusaki, J., Okayasu, M., Yamauchi, S. and Fueki, K.J. 1992. *Journal of the Solid State Chemistry* 99: 166.
- Narayanan, S.R., Valdez, T.I., Rohatgi, N., Chun, W. and Halpert, G. 1998. Fuel Cell Seminar, Abstracts, Palm Springs, CA, USA.
- Narayanan, S.R., Clara, F. and Valdez, T.I. 2001. Development of a miniature direct methanol fuel cell system for cellular phone applications. *In: Proceedings of the Symposium on Direct Methanol Fuel Cells, the 199th Electrochemical Society Proceedings Series*, Princeton, NJ, USA.
- Post, M.L., Yang, D., Du, X. and Kassam, Z. 1999a. Proceedings of the Materials Research Society, Boston, MA, Abstract LL7.1.
- Post, M.L., Tunney, J.J., Yang, D., Du, X. and Singleton, D.L. 1999b. Material chemistry of perovskite compounds as chemical sensors. *Sensors and Actuators B: Chemical* 59(2): 190-194.
- Takeda, Y., Kanno, K., Takada, T., Yamamoto, O., Takano, M., Nakayama, N. and Bando, Y. 1986. Phase relation in the oxygen nonstoichiometric system, SrFeO_x ($2.5 \leq x \leq 3.0$). *Journal of the Solid State Chemistry* 63(2): 237-249.
- Tofield, B.C., Greaves, B.C. and Fender, B.E.F. 1975. The $\text{SrFeO}_{2.5}$ - $\text{SrFeO}_{3.0}$ system evidence of a new phase $\text{Sr}_4\text{Fe}_4\text{O}_{11}(\text{SrFeO}_{2.75})$. *Materials Research Bulletin* 10:737-746.
- Tunney, J.J. and Post, M.L. 2000. The electrical conductance of $\text{SrFeO}_{2.5+x}$ thin films. *Journal of Electroceramics* 5(1): 63-69.