Key Engineering Materials Vols. 368-372 (2008) pp 263-264
Online available since 2008/Feb/11 at www.scientific.net

doi:10.4028/www.scientific.net/KEM.368-372.263

Limiting Current Oxygen Sensors with LSM as Dense Diffusion Barrier

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Keywords: Solid electrolyte; Oxygen sensor; Limiting current; Dense diffusion barrier

Abstract. A thick film type of limiting current oxygen sensor which uses yttria (8% mol) stabilized zirconia (YSZ) as oxygen ion conducting solid electrolytes and dense $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as diffusion barrier was developed successfully. The oxygen sensor showed excellent performance at oxygen concentrations ranging from 0 to 10 ppm. The advantages of the sensor are simple construction, low cost and potential long term stability.

Oxygen sensor has extensively used in automobile industry to monitor exhaust composition and control the air-to-fuel ratio, thus reducing pollutants emission and improving fuel economy. Now there are two kinds of physical diffusion barriers used in limiting current oxygen sensors. One is a cavity with a small hole, the other is a porous ceramic layer on the cathode [1, 2]. However, they have some problems, for example, high cost, easy occluding of the apertures and size change of the hole when used for a long time. The problems can be solved when mixed conduction membrane of election-oxygen ion is used as diffusion barrier [3]. $La_{0.8}Sr_{0.2}MnO_3$ (LSM) is a good mixed electronic-oxygen ion conductor. As the transference of oxygen in mixed conductor is finished by lattice faults, it can mot occur that oxygen permeability changes with using history. Furthermore, because mixed conducting materials has high electronic conduction and no potential exists between interfaces of mixed conductor membrane, the amount of diffusion oxygen only depends on oxygen partial pressure in atmosphere at fixed temperature for a certain material. In the paper, a new type of limiting current oxygen sensor that uses $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as diffusion barrier is developed successfully through a new and effective technology.

$La_{0.8}Sr_{0.2}MnO_3$ (LSM) is fabricated by solid-state reaction. La_2O_3, $MnCO_3$ and $SrCO_3$ powder (AR grade) are mixed according to required ratio and then ball-milled in acetone medium for 12 h. The slurry is dried and calcined at 1623 K for 10 h. Sintered LSM powder is analyzed by X-ray diffraction (XRD). The result is shown in Fig. 1, which indicates that LSM single phase has formed and no other phases exist.

Yttria (8 mol %) stabilized zirconia (YSZ) powder is pressed lightly at first, then added with LSM and YSZ (50 wt %) mix-powders and are pressed together (thickness 5 mm, diameter 10 mm). The

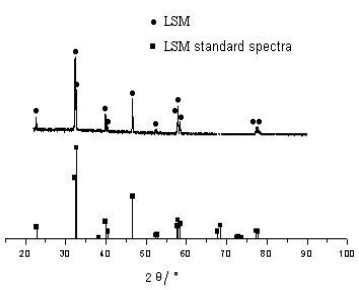

Fig.1 XRD pattern of LSM powders

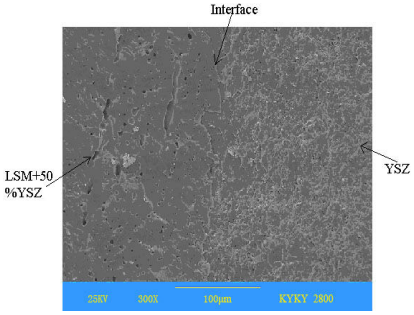

Fig.2 SEM of cross-section of sensor

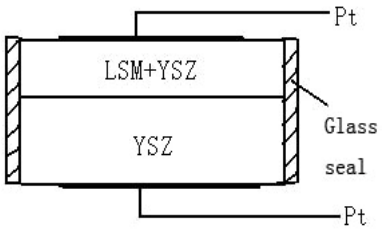

Fig.3 Schematic construction of sensor

pellet is sintered at 1673 K for 6 h. The boundary surface view of YSZ and YSZ+LSM, as shown in Fig. 2, shows that they are boned well and no crackles exist. To prevent oxygen from leaking from the edges of the pellet, glass seal is applied around the circumference of the pellet. Finally, platinum paste is painted on the both surfaces of the sensor and burned at 1073 K for 1 h. The configuration of sensor is shown in Fig. 3.

Output current is measured and recorded at different partial pressure of oxygen and different applied voltage by computer controlling Chi660A electro-chemical workstation at fixed 1073 K. Polarization potentials are controlled at range of 0 to 2.4 V. The O_2/Ar gas mixtures with O_2 concentration varying from 0 to 10ppm were prepared by mixing air and Ar using mass-flow controllers. The flow rate of measuring gas was maintained at 100 cm^3 /min.

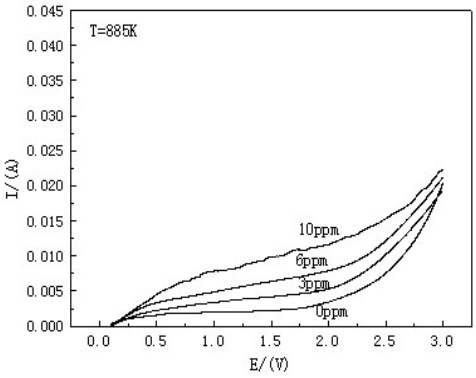

Fig.4 Current-voltage characteristic curves of sensor

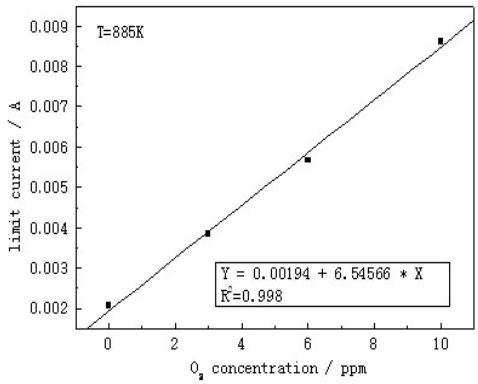

Fig.5 The relation of limiting current with oxygen concentration for sensor

Fig. 4 shows typical current-voltage (I-V) curves of above sensor at different partial oxygen pressure, when potential varies from o to 1.6 V. It can be seen from this figure that sensor's currents increase with applied potentials vary from 0 to 0.4 V and 0 to 0.7 V for low and high oxygen partial pressure. The currents reach mA level, showing that inner resistance of sensor is low and mixed conductor has high oxygen diffusion property. The diffusion-limited currents are constant at oxygen concentration range of 0 to 10 ppm when applied potentials are controlled at 0.7 V to 1.8 V. However, the diffusion-limited currents are enlarged quickly when the applied voltage is elevated. This can be explained that the YSZ is reduced to form more oxygen vacancies.

The relationship of between diffusion-limited current and oxygen concentrations is shown in Fig. 5. A good linear correlation is gotten at the range of measured oxygen concentrations. The related coefficient is about 0.998. The sensor has also displayed good stability at experimental time. To get sensor whole performance, more work need to do, for example, optimized temperature, concentration range, response time, cross-sensibility, reproducibility and so on.

A limited current oxygen sensor successfully fabricated by incorporating YSZ solid electrolytes and dense LSM diffusion barrier. The oxygen sensor showed excellent performance at oxygen concentration ranging from 0 to 10 ppm. The limiting current oxygen sensors need to be optimized further in the future work.

Acknowledgements

Many thanks to the National Natural Science Foundation of China (50572024) and Education Ministry Foundation for Returning Overseas Scholar for supporting the work.

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High-Performance Ceramics V
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