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Liquid metal/metal oxide reference electrodes for potentiometric oxygen sensor operating in liquid lead bismuth eutectic in a wide temperature range

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Abstract

Potentiometric oxygen sensors with LBE/PbO and In/In_2O_3 reference electrodes coupled with yttria partially stabilized zirconia (YPSZ) have been developed for use in liquid lead-bismuth eutectic (LBE) over the temperature range from 200 to 450 °C. The performance of sensors with LBE/PbO and In/In_2O_3 reference electrodes was evaluated comparing the oxygen activity measured in oxygen saturated LBE (from 200 to 450 °C) with these sensors to the one measured by sensors with Bi/Bi_2O_3 and air/LSM (strontium-doped lanthanum manganite) electrodes, using same solid electrolyte and measurement setup. The sensors with LBE/PbO and In/In_2O_3 reference electrode performed well down to 200 °C while the sensor with Bi/Bi_2O_3 showed significant deviations at 200 °C.
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Keywords: Potentiometric oxygen sensor; Lead-bismuth eutectic (LBE); MYRRHA

1. Introduction

Since 1998, SCK•CEN has been designing a multipurpose Accelerator Driven System (ADS) for R&D applications, called MYRRHA (Multi-purpose hybrid research reactor for high-tech applications), which consists of

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a proton accelerator delivering its beam to a liquid lead-bismuth eutectic (LBE) spallation target that in turn couples to a sub-critical fast core, also cooled with LBE. Active control and monitoring of oxygen content in LBE is one of key technologies for safe operation of MYRRHA.

In order to prevent precipitation of PbO and maintain a protective oxide layer on the structural material surfaces, the oxygen activity should be monitored and controlled over the entire temperature range designed for MYRRHA (200 °C - 450 °C).

Potentiometric oxygen sensors using air/Pt and Bi/Bi_2O_3 reference electrodes coupled with yttria partially stabilized zirconia (YPSZ) have been widely used and tested for LBE systems. However, those sensors showed an operating temperature limit of about 300 °C. Although the superiority of oxygen sensors using air/perovskite oxides reference electrode compared to air/Pt and Bi/Bi_2O_3 reference electrodes was demonstrated at low temperatures [1], the risk of contamination of LBE in case of sensor rupture forces to use a sealed reference electrode for MYRRHA. The oxygen sensors with Bi/Bi_2O_3 reference electrode present significant deviation from temperatures below the melting temperature of Bi, suggesting that reference electrodes using liquid metal having a lower melting temperature than that of Bi might be superior.

In this study, the performance of oxygen sensors with In/In_2O_3, LBE/PbO reference electrodes was investigated in oxygen saturated LBE (LBE/PbO equilibrium) over the temperature range from 450 °C to 200 °C. The dissolved oxygen activity in oxygen saturated LBE measured with these sensors was compared to the one measured by sensors with Bi/Bi_2O_3 and air/ LSM (strontium-doped lanthanum manganite) as reference electrode.

2. Experimental

2.1. Fabrication of oxygen sensors

The M/M.O. (metal/metal oxide) reference electrode sensors were fabricated using In (99.99%, Alfa Aesar), In_2O_3 (99.99%, Alfa Aesar), Bi_2O_3 (99.99%, Mateck) powders and Pb (99.999%, Alfa Aesar) and Bi granules (99.997%, Alfa Aesar) as raw material. One end closed tubes of yttria partially stabilized zirconia (YPSZ, Friatec), 6 mm in outer diameter and 3 mm as inner diameter, were used as solid electrolyte material. As reference, a mixture of metal and corresponding metal oxide were applied to the tip of the tubes to guarantee an equilibrium oxygen activity at given temperature. The reference electrode was contacted to a Mo wire (99.95%, Alfa Aesar) connected to a mineral insulated signal cable (ThermoCoax).

Fig. 1 shows a schematic drawing and a picture of an oxygen sensor with M/M.O. reference electrode.

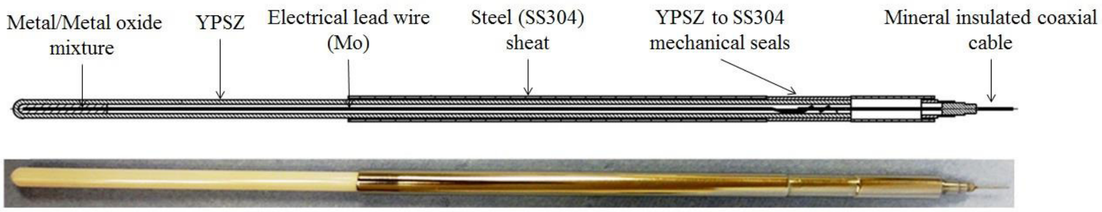

Fig. 1. Schematic drawing (upper) and picture (lower) of a metal/metal oxide reference electrode sensor.

The air/LSM reference electrode sensor was made as described in [1].

2.2. Experimental setup

To compare the performance of the sensors with different reference electrodes, the difference of potential (ΔV) arising between the reference electrode and oxygen saturated LBE was measured over the temperature range from 200 to 450 °C.

The galvanic cell used in this study can be represented as follow:

- SS304, LBE, PbO |YPSZ| air, LSM, SS304
- SS304, LBE, PbO |YPSZ| Bi, Bi_2O_3, Mo
- SS304, LBE, PbO |YPSZ| In, In_2O_3, Mo
- SS304, LBE, PbO |YPSZ| LBE, PbO, Mo

The oxygen sensors were immerged in about 350 mL of LBE contained in an alumina crucible which was inserted in a stainless steel pot wrapped with electrical heaters. The gap between the outer SS pot and the alumina crucible was filled with LBE to decrease the thermal gradient. The cover of the cell was kept open to air.

The ΔV was measured at six different temperatures from 450 to 200 °C with 50 °C steps. The temperature was kept constant for 10 hours for each step while during transients, the temperature was decreased at a rate of 0.1 °C/min to keep the equilibrium LBE/PbO as close as possible also during transients.

The ΔV was measured every 30 seconds using an Agilent voltmeter 34972A and selecting a high input resistance (> 10GΩ).

3. Results

Fig. 2 shows the ΔV measured by the oxygen sensors with air/LSM, Bi/Bi_2O_3, In/In_2O_3 and LBE/PbO reference electrodes in oxygen saturated LBE. For each oxygen sensor, the measured ΔV (solid line) was compared to an expected ΔV (dotted line), which is a linear extrapolation from data measured at 450 and 400 °C. The average values were calculated using data measured in the last three hours at 450 and 400 °C.

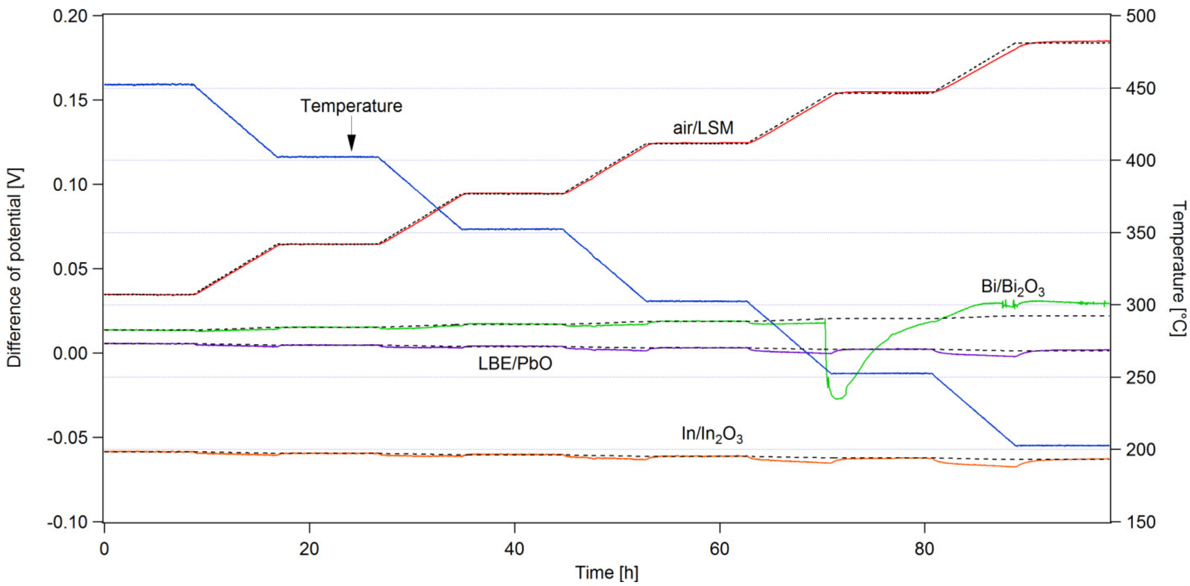

Fig. 2. Measured ΔV by sensors with air/LSM (red line), Bi/Bi_2O_3 (green line), LBE/PbO (purple line) and In/In_2O_3 (red line) reference electrodes compared to linear trend (dotted black line) extrapolated using ΔV measured at 450 and 400 °C. The sensor with Bi/Bi_2O_3 (green line) deviates significantly from temperature lower than 300 °C.

In order to compare the performance of different reference systems, the dissolved oxygen activity in oxygen saturated LBE ($a_{o,w}$) was calculated from the difference of potential (ΔV) measured by each sensor according to the Nernst equation:

$$\Delta V = \frac{RT}{2F} \ln\left(\frac{a_{O,ref}}{a_{O,w}}\right) \tag{1}$$

where R is the gas constant (8.3145 J $K^{-1}mol^{-1}$), T is the absolute temperature (K), F is the Faraday constant (96,485.34 C mol^{-1}), $a_{o,ref}$ is the oxygen activity at the reference side and ΔV is the measured difference of potential (V).

For the sensor with air/LSM reference electrode, the activity at the reference side is defined:

$$a_{O,ref} = \left(\frac{p_{O_2,air}}{p^0} \right)^{0.5} \quad (2)$$

where $p_{O2,air}$ is the oxygen partial pressure in air (0.20946 in dry air) and p^0 is the reference pressure (1 bar).

For M/M.O. reference systems, the oxygen activity at the reference side is determined by the redox equilibrium of the following chemical reaction at constant temperature:

$$xM_{(l)} + y[O]_{inM} = M_xO_y \quad (3)$$

Therefore, the dissolved oxygen activity of the M/ M.O. mixture can be calculated by the following expression:

$$a_{O,ref} = \exp\left(\frac{\Delta_f G^0{}_{M_xO_y}}{yRT} \right) \quad (4)$$

where $\Delta_f G^0_{MxOy}$ is the standard molar Gibbs free energy of formation of the metal oxide (J mol^{-1}).

Fig. 3 shows the dissolved oxygen activity measured in oxygen saturated LBE by the sensors used in this study.

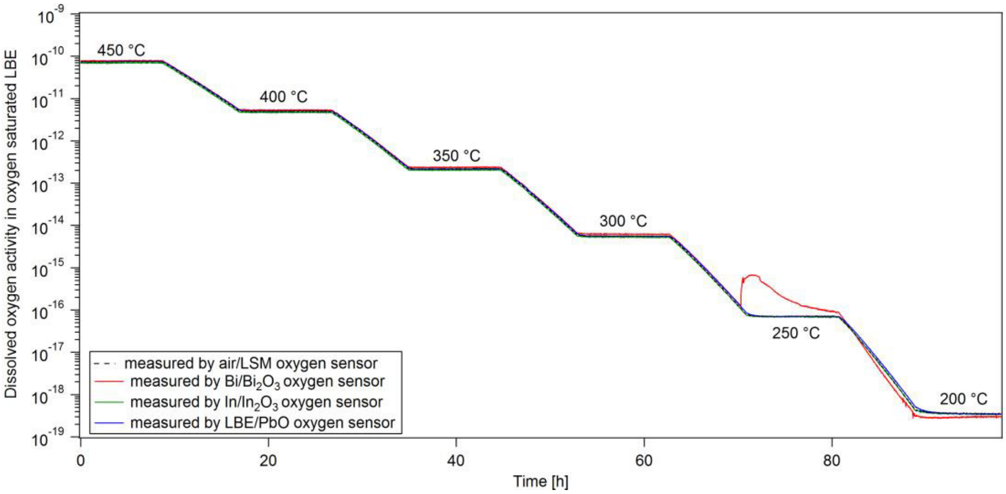

Fig. 3. Dissolved oxygen activity measured in oxygen saturated LBE by sensors with air/LSM (dotted line), Bi/Bi_2O_3 (red line), In/In_2O_3 (green line) and LBE/PbO (blue line) reference electrodes over the temperature range from 450 to 200 °C.

4. Conclusions

Potentiometric oxygen sensors with In/In_2O_3 and LBE/PbO as reference electrode measure properly in LBE over the temperature range from 450 to 200 °C.

References

[1] J.Lim, G. Manfredi, A. Marïen, J. Van den Bosch, Sensors and Actuators B: Chemical 188 (2013) 1048-1054.