

1-22-2003

Calibration of YSZ Sensors for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic

Xiaolong Wu

University of Nevada, Las Vegas

Ramkumar Sivaraman

University of Nevada, Las Vegas

Ning Li

Los Alamos National Laboratory

Wei Hang

Los Alamos National Laboratory

T. W. Darling

Los Alamos National Laboratory

Follow this and additional works at: https://digitalscholarship.unlv.edu/hrc_trp_sciences_materials

 [next page for additional authors](#) Part of the [Materials Chemistry Commons](#), [Nuclear Engineering Commons](#), and the [Oil, Gas, and Energy Commons](#)

Repository Citation

Wu, X., Sivaraman, R., Li, N., Hang, W., Darling, T. W., Jiang, Y., Yim, W., Fu, B. (2003). Calibration of YSZ Sensors for the Measurement of Oxygen Concentration in Liquid Pb-Bi Eutectic. 1-6.

Available at: https://digitalscholarship.unlv.edu/hrc_trp_sciences_materials/154

This White Paper is protected by copyright and/or related rights. It has been brought to you by Digital Scholarship@UNLV with permission from the rights-holder(s). You are free to use this White Paper in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you need to obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/or on the work itself.

This White Paper has been accepted for inclusion in Transmutation Sciences Materials (TRP) by an authorized administrator of Digital Scholarship@UNLV. For more information, please contact digitalscholarship@unlv.edu.

Authors

Xiaolong Wu, Ramkumar Sivaraman, Ning Li, Wei Hang, T. W. Darling, Yingtao Jiang, Woosoon Yim, and Bingmei Fu

CALIBRATION OF YSZ SENSORS FOR THE MEASUREMENT OF OXYGEN CONCENTRATION IN LIQUID Pb-Bi EUTECTIC

Xiaolong Wu¹, Ramkumar Sivaraman¹, Ning Li², Wei Hang², T. W. Darling²,
Yingtao Jiang¹, Woosoon Yim³, Bingmei Fu³

1. Department of Electrical
and Computer Engineering
University of Nevada, Las Vegas
Las Vegas, NV 89154

2. Los Alamos National Laboratory
Los Alamos, NM 87544

3. Department of Mechanical Engineering
University of Nevada, Las Vegas
Las Vegas, NV 89154

ABSTRACT

Although liquid lead-bismuth eutectic (LBE) is a good candidate for coolant in the subcritical transmutation blanket, it is known to be corrosive to stainless steel, the material of the carrying tubes and containers. Such long-term corrosion problem can be prevented by producing and maintaining a protective oxide layer on the exposed surface of stainless steel. For this purpose, it is required to accurately control the concentration of oxygen dissolved in LBE. Currently, YSZ (Yttria Stabilized Zirconia) oxygen sensors, based on an existing automotive oxygen sensor, with molten bismuth saturated with oxygen as the reference, have been selected for oxygen-concentration measurement. The oxygen concentration difference across the solid electrolyte and the resultant oxygen ion conduction inside the electrolyte establishes an electromagnetic force that is used to measure the ppb level concentration of oxygen dissolved in liquid LBE. A set of calibration curves of voltage vs. temperature ranging from 300 °C to 500 °C under various oxygen concentrations in liquid LBE for the YSZ oxygen sensor has been obtained and is presented in this paper. Although the current calibration strategy using the direct injection of hydrogen and oxygen is still inadequate to determine the oxygen concentration in the system, we have found a good candidate for our purpose, which is varying hydrogen to water steam ratio in the system.

1. INTRODUCTION

Due to the relatively high solubility of the major alloying components of steel used in nuclear systems, liquid lead-bismuth can be severely corrosive to steel. The long term reliability of piping made of such material is determined by its resistance to being dissolved, eroded and corroded by the LBE liquid. If a protective layer of oxide can be maintained on the surface of the stainless steel tube exposed to liquid LBE [1], the resistance of piping can be greatly enhanced. Since the oxygen chemistry is

sufficiently well known, by controlling the temperature and the concentration of oxygen dissolved in liquid LBE, we can maintain the oxide layer. Thus, it is of critical importance to accurately measure the oxygen-concentration in LBE, after which the active control of the oxygen concentration becomes possible.

Measurement of oxygen levels in the liquid lead-bismuth can be performed by measuring the voltage developed across doped zirconia ceramic when a difference in oxygen concentration also exists across them. The material is relatively expensive and construction of reliable temperature-cycling joints is difficult. The automobile industry has many years of experience in this ceramic for exhaust line oxygen sensors. These commercially available elements have many advantages: consistent materials properties, a convenient conical shape, and a formed flange for mechanically holding and sealing the element. We have used such an automobile-style YSZ oxygen sensor unit to measure oxygen levels in LBE test loop [8]. In this paper, we will provide information regarding how this YSZ sensor can be used in our system and present here our oxygen sensor calibration results.

The rest of the paper is organized as follows. Section 2 introduces the solid electrode oxygen sensor and its working mechanism. Section 3 presents our sensor calibration strategies. Section 4 describes the experimental setup and the experiment procedure in detail. Section 5 reports the preliminary results. And section 6 provides the conclusions and the corresponding discussion.

2. OXYGEN SENSORS

2.1 Solid Electrolyte Materials

The measurement of relative oxygen concentration in liquid metals using solid electrolyte membranes is well established [2] [3]. Solid electrolytes are materials, which are permeable to specific ions. In the case of a sintered ceramic zirconia, ZrO_2 , O^{2-} ions may pass through the solid

from high concentration side to low concentration side if they have sufficient thermal energy. The oxygen ions move by hopping between oxygen vacancy sites. These sites are species-specific – utilized only by oxygen ions. The energy needed to hop between these sites is reduced by stabilizing (or partially stabilizing) the crystal structure of ZrO_2 into cubic or monolithic structure by the addition of 8-18% yttria, Y_2O_3 . This is usually called YSZ (Yttria Stabilized Zirconia) or partially stabilized Zirconia (PSZ) [2]. YSZ/PSZ is readily available in the form of powder or sintered closed end tubes. A closed end tube is a useful form for immersion in liquid LBE, but the high temperature, and the temperature gradients, in LBE case introduce problems with leak-tight seals using either gaskets sealing to a circumference of a cylinder, or with ceramics-metal joints.

2.2 Principles of Operation

Because the hot solid electrolyte membrane is porous to oxygen, an imbalance in the oxygen concentration will cause oxygen to migrate so as to equalize the concentrations on each side. Oxygen on higher concentration side will “pick up” two electrons to become ions, travel through the YSZ and re-formed into a neutral molecule at lower concentration surface where they will “deposit” two electrons [3].



A metallic connection is used for sourcing and sinking electrons, and chemically catalyzing the reaction shown above. In liquid metals, a certain amount of the dissolved oxygen exists as ions, and thereby liquid metals do not need the catalytic action of Pt – just as well, liquid LBE dissolves Pt. The liquid metal is a good connection to YSZ, both for making electrical connection to voltmeters and providing the ions to pass through YSZ [2].

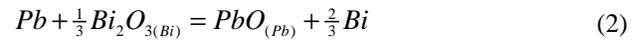
Since we only want to measure relative concentrations, we must have a stable, known oxygen concentration to measure against. The outside of the conical sensor will be immersed in LBE with an unknown oxygen concentration. The inside must be exposed to the reference. One reference is when the inside is coated with porous Pt, we then can use the reasonable stability of the concentration of atmospheric oxygen ~21% as a reference. This has the advantage of being able to be mounted at any angle, and the disadvantage of requiring a vent to the atmosphere (potential LBE leak path), and of having a reference where local concentration variations may occur.

The oxygen sensor used in our case, shown in Fig. 1, employs another reference for measuring oxygen concentration. The inside of the cone contains liquid metal (Bi) and no Pt coating is needed. If the liquid metal, Bi, is

in equilibrium with chunks of its solid oxide, the dissolved oxygen in the liquid will have a known saturation value, depending on the temperature. This saturation value can serve as a good reference. The advantages of using liquid metal saturated with bismuth oxide are having a stable reference and no vent to atmosphere, but it needs a vertical mounting to contain the liquid.

Oxygen must have access to the surface of the YSZ. A common way to achieve this is to insert the sensor into the LBE loop, so that only the zirconia electrolyte is in contact with oxygen molecule present in liquid LBE. Due to the oxygen concentration difference in oxygen-saturated bismuth reference and liquid LBE, there exists a chemical potential difference resulting in the flow of oxygen ions, accumulating charges. When it finally reaches an equilibrium, there is an EMF (electromagnetic force) across the YSZ. The EMF is the measure of the oxygen concentration difference. This way of the measurement is called potentiometric method. The voltage, measured with an “infinite” (10^{11} Ohm) input impedance voltmeter so that no charge leaks off the electrodes into the meter, is then a measure of the concentration difference. The equilibrium voltage associated with the charge built up will be an indicator of the ratio of the concentrations of oxygen on each side of the electrolyte. We assume that the concentration obeys Henry’s law and the activity is the ratio of the actual oxygen concentration to the saturated state.

For the system of Pb, PbO, oxygen permeable solid electrolyte, Bi and Bi_2O_3 (saturated-exposed to the air), the reaction is



The transport of ions is a thermally activated process, which does not become feasible until the temperature of the solid electrode is greater than about 350 °C, which is in the operating temperature range of the LBE loop system. Above this temperature, the potential difference across the electrode is calculated from the Nernst equation [3] which assumes (i) a perfect porous membrane, (ii) perfect electron transfer at interfaces, (iii) pure ionic conduction, and (iii) no ohmic contributions (zero current).

$$E = E_{PbO}^0 - E_{Bi_2O_3}^0 - \frac{RT}{2F} \ln \frac{a_{Bi}^{2/3} a_{PbO}}{a_{Pb} a_{Bi_2O_3}^{1/3}}$$

$$= \frac{1/3\Delta F_{Bi_2O_3}^0 - \Delta F_{PbO}^0}{2F} - \frac{RT}{2F} \ln a_{PbO} \quad (3)$$

Where (i) $E_{PbO}^0 - E_{Bi_2O_3}^0$ is the difference in the free energies of formation of the bismuth and lead oxides at the temperature T, in volts; (ii) F and R are the Faraday and

ideal gas constants, respectively; (iii) T is the absolute temperature; and (iv) a_x is the activity of species X . These activities are assumed to be simply related with the corresponding oxygen concentrations by Henry's law. The values for the free energies were taken from the Oxide Handbook [4].

2.3 The Oxygen Sensor Used in Our Experiments

The oxygen sensor used in our experiments is manufactured by Delphi, a GM spinoff company. We have special ordered elements with no Pt coating and with Pt coating on the inside only. The cost is approximately \$8 each, which is shown in Fig. 1. The sensors actually operate at temperature above 360 °C as Fig. 2 indicates. Above 360 °C, despite the existence of an offset, the behavior of the sensor agrees with the Nernst Equation prediction [8].

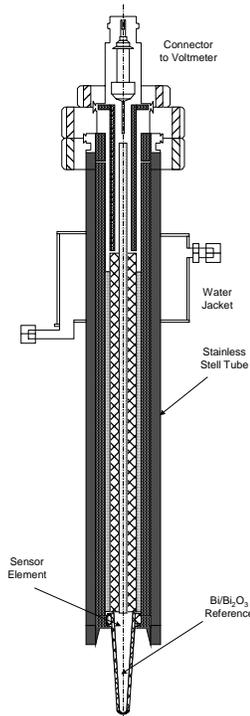


Fig.1 Schematic Drawing of the Oxygen Sensor in Our Experiment.

The zirconia ceramic used as the sensor element is a strong but brittle material. If for any reason the sensor, or any seal in the module should break and allow liquid LBE out of the normal flow of the loop, the LBE must be contained and any potential flow paths minimized. Design or procedures thus should minimize the possibility of any brittle section being subjected to thermal shocks.

In addition, the sensor and seals should have a good life expectancy under operating conditions and thermal cycling of the loop. Provision should be made to replace sensor elements without major cutting or welding operations. The sensor module should be made with materials and thickness that will be not be adversely affected by the temperature in the loop or deteriorated by prolonged contact with liquid LBE [8].

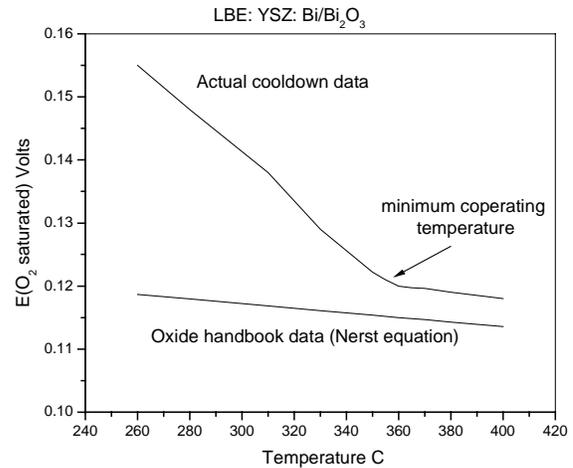


Fig. 2 Operating temperature for the YSZ sensor

The oxygen sensor shown in Fig.1 was developed to meet the requirements listed above. A stainless tube penetrates the loop pipework and is welded in place. The sensor element has a graphite seal at the bottom of the tube so that it protrudes into the LBE flow. The interior of the tube has several concentric tubes of stainless steel and alumina ceramic. This serves as several purposes: (i) the space inside the tube is almost entirely filled, leaving the smallest gaps for LBE leak paths; (ii) the inner tubes serves as push rods to compress the graphite gasket material between the sensor support ring and the tube tip, and between the sensor and the sensor support ring; and (iii) the ceramic insulates the innermost tube and the connection wire (made of Ta, insoluble in most liquid metals), so they can both be used as electrical connections. A standard vacuum flange with copper gasket is welded to the top end. A mating flange seals, and via a spring and the first inner tube, compresses the support ring gasket. A second flange with a high temperature BNC feedthrough also seals with a copper gasket and through a spring and the innermost tube, presses the sensor onto its gasket. Electrical connections are made via the BNC feedthrough to a liquid reference through a Ta wire down the center ceramic tube, or to the Pt metal coating connection through the innermost stainless tube near the flange end. This design provides protection against leaks by freezing any liquid LBE may, in an abnormal circumstance, find its way

into the tube. It also keeps the connection end cool so that BNC cable fitting (inevitably containing plastics) will not be adversely affected by the heat.

2.4 Measurement

Determining the oxygen concentration is impacted by both the liquid metal and the its contacting surface. The liquid metal of interest is Pb-Bi Eutectic, LBE (55% Bi, melting temperature 123.5 °C; boiling temperature 1670 °C). Many metals are soluble at low concentrations, form intermetallics or amalgamate in this liquid. As mentioned earlier, surfaces containing these soluble metals may be protected by an oxide layer, provided that layer can be maintained by a sufficient concentration of oxygen concentration in the LBE. This sets a lower limit on the oxygen concentration in the LBE, below which steel corrosion takes place, corresponding to the maximum value of EMF, E_{max} . From the Oxide Handbook [4], we have

$$E_{max} = 8.17 \times 10^{-5} T + 0.431 [V] \quad (4)$$

An upper limit is set by the concern that we do not wish to have any solid oxides of Pb or Bi formed in the liquid which might clog or damage the system, or which might provide source of oxygen that cannot be easily removed. This corresponds to the minimum value of E EMF, E_{min} . From the Oxide Handbook [4], we have

$$E_{min} = -3.63 \times 10^{-5} T + 0.138 [V] \quad (5)$$

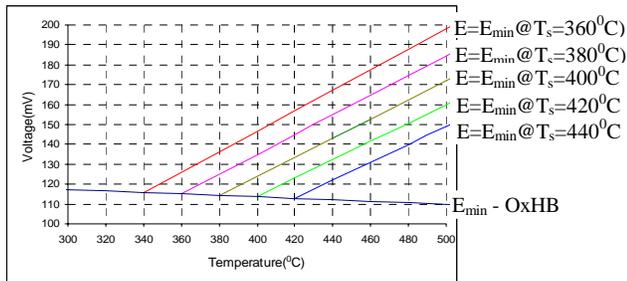


Fig. 3 Voltages at Different Oxygen Concentrations using Eqs. (5) & (6).

From the Henry's law [5], we can convert partial pressure of oxygen to the corresponding dissolved oxygen concentration in liquid LBE. Since the oxygen sensors usually do not work reliably until well above 350°C for the lack of sufficient oxygen diffusion in the solid electrolyte at low temperatures, it would be useful to map out E vs. T for the existence of proper conditions throughout the system. According to [4], the E corresponds to different oxygen saturation levels as,

$$E(T) = -3.63 \times 10^{-5} T - 0.199 + \frac{0.337T}{T_s} [V] \quad (6)$$

Here T_s is the saturation temperature for oxygen. Fig. 3 shows E vs. T curves for various oxygen concentration levels using Eqs. (5) & (6).

3. SENSOR CALIBRATION STRATEGY

Oxygen Sensors used in LBE loop need to measure oxygen concentration in the range of tens of ppb to a few ppm level. There are several ways to control low oxygen concentrations in the system, such as the Direct Injection of Oxygen and Hydrogen Gases [6], and the Injection of Hydrogen and Water Steam Mixtures [7].

Direct injection of oxygen and hydrogen gases is currently used to regulate low oxygen concentrations because the setup and the procedures are simple, and input and output are in forms with easy addition of gas supplies without solid residues [6]. In this method, hydrogen and oxygen are typically mixed with an inert cover gas, helium, to regulate the pressure and, introduced directly into the system. We use the saturation limit (when lead oxide precipitates) and the oxide dissociation limit (typically that of magnetite, Fe_3O_4) for calibration. When oxygen in liquid LBE reaches solubility limit, oxygen thermodynamic activity will reach a "fixed" point. If this happens during addition of oxygen, the continued addition of oxygen will not change the activity. If the LBE temperature decreases slowly, oxygen activity will follow the solubility change, since solubility decreases with decreasing temperature. Knowing the solubility of oxygen in LBE, one can obtain a group of temperature dependent calibration curves of sensor voltages [6].

The low concentration of oxygen in the order of tens of ppt makes it nearly impossible to supply oxygen at the right level directly. However, hydrogen and water system is used as an alternative to solve this problem. A hydrogen and cover gas (He or Ar) mixture passes through a temperature-controlled water bath to pick up water vapor at the desired levels.

In the reaction of



The reaction equilibrium constant is

$$K = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} = \exp\left[-\frac{\Delta F_{H_2O}^0}{RT}\right] \quad (8)$$

It is evident from the above equation, that the ratio of the H_2 and H_2O determines the partial pressure of oxygen.

$$\frac{P_{H_2O}}{P_{H_2}} = P_{O_2}^{1/2} \exp\left[-\frac{\Delta F_{H_2O}^0}{RT}\right] \quad (9)$$

Given the equation (9), by controlling the ratio of P_{H_2O}/P_{H_2} , we can obtain the desired very low O_2 concentration. The resultant hydrogen/steam mixture can either go directly into the LBE system to complete the reaction there, or go through a high-temperature reaction chamber to reach a thermodynamic equilibrium (hence the desired oxygen level) beforehand.

4. EXPERIMENTAL SETUP AND PROCEDURES

Fig. 4 shows the experimental setup. It comprises of an oxygen sensor with its zirconia tip dipped into the liquid LBE in a steel tube. The amount of LBE in the steel tube is approximately 25 kilograms (~ 2.5 liters). The steel tube is tightly sealed from outside atmosphere except for a few gas inlets and outlets.

The loop and the liquid LBE will be maintained at ground potential as closely as possible. In this way, the shell of the BNC feedthrough, connected by a few welds, will be considered as a good ground, and thus it can serve as the voltage reference for the measurement of the charges accumulated at the inside electrode. The inside electrode, liquid Bi, is connected to the center conductor of the BNC. A standard BNC cable will take this signal to a BNC bulkhead connector through the wall of the loop enclosure. From there, another BNC cable will take the signal to the input of an electrometer with $10^{11} \Omega$ input impedance. A low impedance analog output from these instruments will be taken to a digitizing input to be read by the computer control system.

Hydrogen, helium and oxygen are introduced into the system through inlet tubes and the unreacted and residual gases are cleaned out through the exhaust pipes. A Residual Gas Analyzer (RGA) is connected to the system to measure the partial pressure of the gases inside the system. A temperature controller is used to control as well as monitor the temperature of the system. A rocker system is employed for homogenizing the gases in LBE [2].

The experiment is performed by initially setting up the temperature of the system to a high value (as close to $500^{\circ}C$ as possible) and at a specific oxygen concentration, and then decreasing the temperature by $10^{\circ}C$ in about every 20 mins. This procedure is followed until the sensor voltage level reaches E_{min} , below which lead precipitation

occurs. For example, in Fig. 6, curve 1b was obtained by initially setting up the temperature to $480^{\circ}C$ and then decreasing the temperature by $10^{\circ}C$ every ~ 20 minutes. This was followed until the voltage reached E_{min} around $330^{\circ}C$, which means voltage will not decrease anymore, start to increase. The sensor voltage was measured at intervals of ~ 10 seconds throughout the experiment and recorded in LabVIEW program with the corresponding temperature.

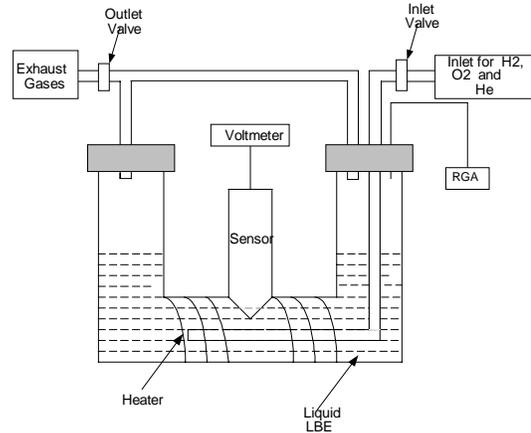


Fig. 4 Experimental Setup for Calibration of Zirconia Sensor

5. RESULTS

Adding hydrogen gas tends to remove dissolved oxygen from the fluid in the form of water vapor, while adding oxygen gas increases the dissolved oxygen content. Hence, helium/6% hydrogen gas is bubbled into the liquid, when we need to clean the dissolved oxygen in LBE liquid where as helium/6% oxygen gas was introduced whenever it is necessary to increase the dissolved oxygen concentration in LBE liquid.

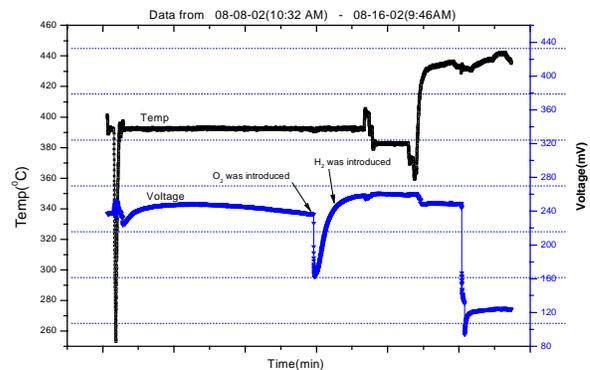


Fig. 5 Voltage Response of Oxygen Sensor to Hydrogen and Oxygen Gas Flows

Fig. 5 shows the voltage response of our oxygen sensor in a test loop. From the experimental data, we have found that: (i) when oxygen gas was introduced into the liquid, the voltage responded immediately and decreased very quickly; however, (ii) when hydrogen was introduced into the liquid, the voltage responded very slowly. In addition, our results showed that the cleanup process is much less efficient than the oxidation process, suggesting that initial cleaning of LBE would be advantageous. Also it seems that our experimental data and the calculated values based on the Eq. (3) are close, but not entirely accurate, suggesting the importance of calibration.

Comparing the experimental curves of Fig. 6 with the one obtained theoretically (Fig. 3), we have also found that their curve slopes are almost the same, both in the range from 0.33 to 0.5. This indicates that the YSZ sensors we used are of high sensing quality under our experimental conditions, which satisfy the requirements set by Eq. (3). The turning points on the curves clearly depict the region at which the oxygen saturation (a little above the theoretical calculation) occurs. These analyses suggest that our experimental results be consistent with theoretical predictions. We have used two sensors in the experiment. In Fig. 6, curves 1a, 2a, 3a are calibration curves for the first sensor, and curves 1b, 2b, 3b, 4b for the second sensor. Overlapping of the calibration curves (3a & 3b) indicates the consistency of the sensors of the same design.

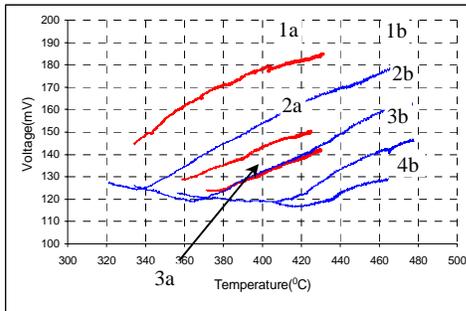


Fig.6 Voltages at Different Oxygen Concentrations (Experimental Results)

6. CONCLUSIONS

From the experiments done so far, we have found that it is difficult to produce the correct level of oxygen in the system using current oxygen control method of direct injection of oxygen and hydrogen gases because of extreme low level of the oxygen concentration. In particular, the theoretically calculated oxygen partial pressure level in the system is around 10^{-30} torr. As mentioned in Section 4, a RGA system has been used to measure all the partial pressure in the cover gas. But the

precision of RGA system only can be around 10^{-10} torr. Therefore, it is impossible to use this data collected from RGA oxygen partial pressure readings to further calculate the concentration of oxygen dissolved in the LBE liquid, which is unfortunately required in the calibration.

Our current experiments aimed at choosing a possible oxygen sensor for the measurement of very low oxygen concentration in LBE. Although we did not successfully determine the oxygen concentration in our calibration set-up, we have found a good candidate for our purpose. In order to control oxygen concentrations at the required low levels, we will continue to perform calibrations by varying hydrogen to water steam ratio in the system, which has been discussed in Section 3. In this way, we can easily adjust the partial pressures of hydrogen and water steam as long as keeping their ratio low enough to achieve desired low oxygen pressure [5]. In addition, calibrations at the other end for oxide dissociation limit (typically that of magnetite, Fe_3O_4) will be conducted. Furthermore, we are planning to cross-calibrate sensors of different electrodes such as In/ InO_2 or Pt/air.

7. REFERENCES

- [1] F. BARBIER, G. BENAMATI, C. FAZIO, and A. RUSANOV, "Compatibility tests of steels in flowing liquid lead-bismuth," *J. Nuc. Mat.* 295, 149-156, (2001)
- [2] Los Alamos Laboratory Experimental Operation Manual
- [3] E. M. Logothetis and R. E. Htrick, "High-Temperature Oxygen Sensors Based on Electrochemical Oxygen Pumping," Scientific Research Laboratories, Ford Motor Company, Dearborn, MI 48121-2053
- [4] G.V. Samson (Ed.), *The Oxide Handbook*, 2nd Ed., IFI/Plenum: New York, (1982).
- [5] N. Li, "Active Control of Oxygen in Molten Lead-Bismuth Eutectic Systems to Prevent Steel Corrosion and Coolant Contamination," *J. Nuc. Mat.* 300, 73-81, (2002)
- [6] N. Li and T. W. Darling, "Oxygen Control Methodology and Sensor Calibration Strategy," LANL, May 30, (2002).
- [7] V.A. Gulevsky, et al. "Application of Hydrogen/Water Vapor Mixtures in Heavy Coolant Technology", in the proceeding of Heavy Liquid Metal Coolants in Nuclear Technology (HLMC-98), Obnisk: SSC RF – IPPE, Vol.2, 668-67, (1992)
- [8] T. W. Darling and N. Li, "Oxygen Concentration Measurement in Liquid Pb-Bi Eutectic," LANL.