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Application of Electromotive Force Measurement in Nuclear Systems Using Lead Alloys

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1. Introduction

Liquid lead and lead-bismuth eutectic (LBE) are promising candidate materials as coolant of fast reactors with improved safety because of their good thermal-physical and chemical properties. Liquid LBE is also a primary candidate material for high-power spallation targets and coolant of accelerator driven systems (ADSs) for transmutation of long-lived radioactive wastes. In order to apply these liquid lead and LBE to nuclear systems, development of systems for controlling oxygen concentration in the liquid mediums is one of important research subjects (Gromov et al., 1999; Shmatko & Rusanov, 2000; OECD/NEA Handbool, 2007). Liquid lead and LBE are corrosive for steels at high temperatures and likely to cause plugging due to PbO formation in low-temperature components of systems. It is generally accepted that maintaining a certain level of oxygen concentration in them is crucial from the viewpoints of mitigating corrosion attack at high-temperature parts and avoiding PbO formation at low-temperature parts. The active oxygen control within the range between Fe_3O_4 and PbO formation has been proposed (Shmatko & Rusanov, 2000; Li, 2002; OECD/NEA Handbool, 2007).

Effective control of the oxygen concentration requires devices for removing and adding oxygen in liquid lead alloys and oxygen sensors for monitoring the oxygen concentration. It is essential to measure oxygen concentration correctly in lead alloys online for the active oxygen control. Electromotive force measurement using oxygen sensors with a solid electrolyte is a useful means to measure oxygen concentration in liquid lead alloys. Oxygen sensors employing yttria-stabilized zirconia (YSZ) and magnesia-stabilized zirconia (MSZ) as a solid electrolyte enable us to measure oxygen concentration in lead alloys. While oxygen sensors using YSZ as a solid electrolyte and Pt/gas as a reference system are often used in automobile industries, the operating temperature of the sensors is generally rather high. It has been reported that oxygen sensors were used in liquid lead and LBE in Russia where research on nuclear systems using them has been conducted for a long term (Gromov et al., 1999; Shmatko & Rusanov, 2000). The special sensor using YSZ as a solid electrolyte and Mo/Bi-Bi₂O₃ as a reference system gave accurate measurement of oxygen concentration and long service lifetime (Shmatko & Rusanov, 2000). Recently, oxygen sensors for use in liquid lead alloys have been manufactured and examined worldwide.

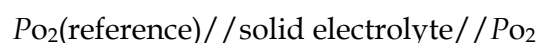
Konys et al. (Konys et al., 2001, 2004) and Schroer et al. (Schroer et al., 2011) showed that YSZ sensors using a Pt/air reference electrode and a Mo/Bi-Bi₂O₃ reference electrode were promising in LBE as a result of tests of sensors using Pt/air, Mo/Bi-Bi₂O₃ and Mo/In-In₂O₃ reference electrodes. Furthermore, it was reported that the Pt/air reference electrode sensor exhibited better reliability and longer lifetime than the Mo/Bi-Bi₂O₃ reference electrode (Konys et al., 2004). Courouau et al. (Courouau et al., 2002a, 2002b; Courouau, 2004) mainly used the YSZ sensor with the Mo/Bi-Bi₂O₃ reference electrode as a result of tests of several Mo/metal-metal oxide electrodes. Calibration was also conducted for the Mo/Bi-Bi₂O₃ reference electrode sensors manufactured at the laboratory scale (Courouau et al., 2002b). The calibration method firstly proposed by Konys et al. (Konys et al., 2001) is based on measurement of electromotive force (EMF) of the oxygen sensor following temperature variation under the condition close to oxygen saturation in LBE. Calibration methods using Co/CoO or Fe/Fe-oxide equilibrium in liquid LBE besides Pb/PbO equilibrium (oxygen-saturated condition) were also attempted (Schroer et al., 2011). The YSZ sensors with the Mo/Bi-Bi₂O₃ reference electrode have been manufactured and used by other researchers (Li, 2002; Kondo et al., 2006; Num et al., 2008). Although sensors with the Mo/In-In₂O₃ reference electrode have been also developed, the temperature range where measured EMF values agree with theoretical values in the calibration test is very narrow (Konys et al., 2001; Courouau, 2004; Fernandez et al., 2002; Colominas et al., 2004). Furthermore, experience has been reported on use of Russian sensor with the Bi-Bi₂O₃ reference and sensors with the In-In₂O₃ reference in liquid Pb-Bi or liquid Pb (Foletti et al., 2008).

The following two problems have been pointed out in case of using the oxygen sensor with the Mo/metal-metal oxide reference electrode: this type of sensor often exhibits time drift that EMF values change with increase in service time (OECD/NEA Handbool, 2007) and measured EMF values disagree with the theoretical ones (Konys et al., 2001; Colominas et al., 2004). We have also tested YSZ sensors using Pt/air reference and Mo/Bi-Bi₂O₃ reference electrodes in LBE. We had experience that even the sensor with the Pt/air reference electrode exhibited incorrect EMF values in LBE after long-term use as a reliable oxygen sensor. Investigation of the cause of the incorrect outputs and re-activation of the Pt/air reference sensor was reported (Kurata et al., 2010). Importance of interface reaction at electrode/medium and electrocatalyst was pointed out in measurement of electromotive force using YSZ oxygen sensors. Furthermore, calibration methods with high reliability and convenience were required for oxygen sensors for use in liquid lead alloys.

In this chapter, the EMF measurement using the YSZ sensor with the Pt/gas reference system is investigated from basic to practical viewpoints together with re-activation treatments of the YSZ sensor. In addition, the usage record of the YSZ sensors with the Pt/air reference system for a long time and situation of oxygen control in liquid LBE in a static corrosion apparatus are described.

2. Theory of oxygen concentration measurement

Figure 1 shows a principle diagram for measurement of oxygen concentration using a solid electrolyte. A solid electrolyte separates two domains characterized by different oxygen partial pressures. When the electrolyte is an oxygen-ion (O²⁻) conductor, an electrochemical galvanic cell using a solid electrolyte is presented as follows:



where $P_{O_2}(\text{reference})$ is the oxygen partial pressure at the reference electrode and P_{O_2} is the oxygen partial pressure at the working electrode. The EMF is formed across the solid electrolyte between the different oxygen partial pressures. The EMF, E is expressed as follows according to the Nernst equation:

$$E = \frac{RT}{4F} \ln \frac{P_{O_2}(\text{reference})}{P_{O_2}} \quad (1)$$

where R is the gas constant, T temperature and F the Faraday constant. When the gas containing a given oxygen concentration is used at the reference electrode side, the oxygen partial pressure at the working electrode, P_{O_2} can be calculated using the Eq. (1). The EMF can be measured using a voltmeter shown in Fig.1. A voltmeter with high impedance is recommended in measurement using solid electrolyte sensors.

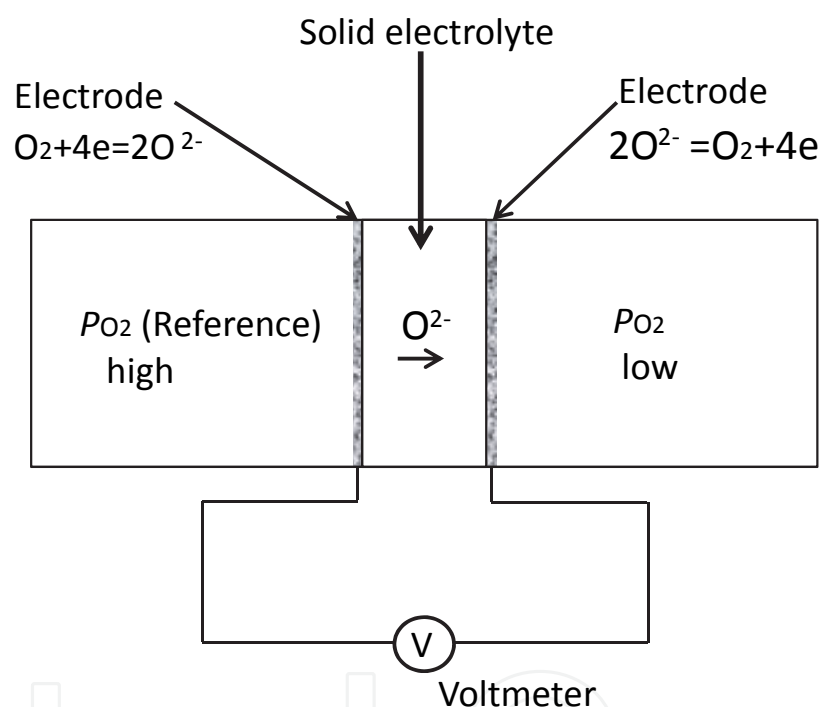


Fig. 1. Principle diagram for measurement of oxygen concentration using a solid electrolyte.

Figure 2 shows a schematic diagram of an oxygen sensor and interface reaction in measurement of oxygen concentration in liquid LBE using YSZ as a solid electrolyte and Pt/gas reference electrode. The following interface reaction occurs on porous Pt as electrocatalyst at the YSZ surface in the reference electrode side:



Type 304SS was used as a working electrode in liquid LBE. Since oxygen dissolves into liquid LBE as O atom, the following interface reaction occurs at the YSZ surface in the liquid LBE side:



The oxygen activity, a_o in equilibrium with an oxygen pressure P_{O_2} is written assuming that dissolution of oxygen into liquid LBE obeys the Henry's law:

$$a_o = \gamma_o C_o = \frac{C_o}{C_o^s} = \left(\frac{P_{O_2}}{P_{O_2}^s} \right)^{\frac{1}{2}} \quad (4)$$

where γ_o is an activity coefficient, C_o the oxygen concentration in LBE, C_o^s the saturated oxygen concentration in LBE and $P_{O_2}^s$ the oxygen concentration in gas in equilibrium with oxygen-saturated LBE. The activity a_o becomes unity when the oxygen dissolved in LBE attains the level of saturation ($C_o = C_o^s$). The saturated oxygen concentration in LBE is calculated using the following Orlov's equation (Gromov et al., 1999):

$$\log C_o^s (wt\%) = 1.2 - \frac{3400}{T} \quad (5)$$

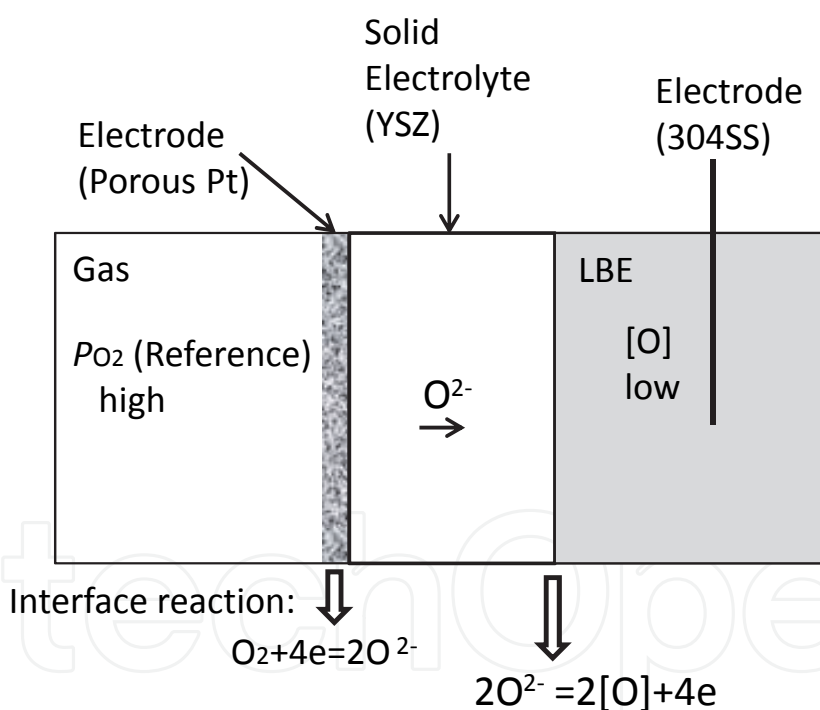


Fig. 2. Reaction at interfaces of solid electrolyte of an oxygen sensor.

Figure 3 shows a schematic diagram to measure oxygen concentration in liquid LBE using two types of oxygen sensors. Oxygen sensors using YSZ as a solid electrolyte and Pt/gas (a) or Mo/Bi-Bi₂O₃ (b) as a reference system were used in this study. When measurement was conducted in LBE, air was used as the reference gas in Pt/gas reference system. The 304SS rod was used as an electrode immersed in LBE. Therefore, the system for measurement in LBE is represented by Pt/air//YSZ//LBE/304SS or Mo/Bi-Bi₂O₃//YSZ//LBE/304SS. The relationship between the EMF and the oxygen concentration in LBE has been calculated for

these two reference electrode sensors using standard Gibbs energy of PbO and Bi₂O₃ (Courouau et al., 2002a; Konys et al., 2004). The equation derived by Courouau et al. (Courouau et al., 2002a) was used in this study.

For Pt/air reference sensor

$$E_{\text{Saturation}} = 1.129 - 5.858 \times 10^{-4} T \quad (6)$$

$$E = 0.791 - 4.668 \times 10^{-4} T - 4.309 \times 10^{-5} T \ln C_o \quad (7)$$

For Mo/Bi-Bi₂O₃ reference sensor

$$E_{\text{Saturation}} = 0.128 - 6.368 \times 10^{-5} T \quad (8)$$

$$E = -0.210 + 5.538 \times 10^{-5} T - 4.309 \times 10^{-5} T \ln C_o \quad (9)$$

Thermoelectric voltages occur between Mo wire and austenitic stainless steels such as 304SS in measurement using the Mo/Bi-Bi₂O₃ reference electrode sensor. The influence of the thermoelectric voltages on measurement was investigated in detail (Schroer et al., 2011).

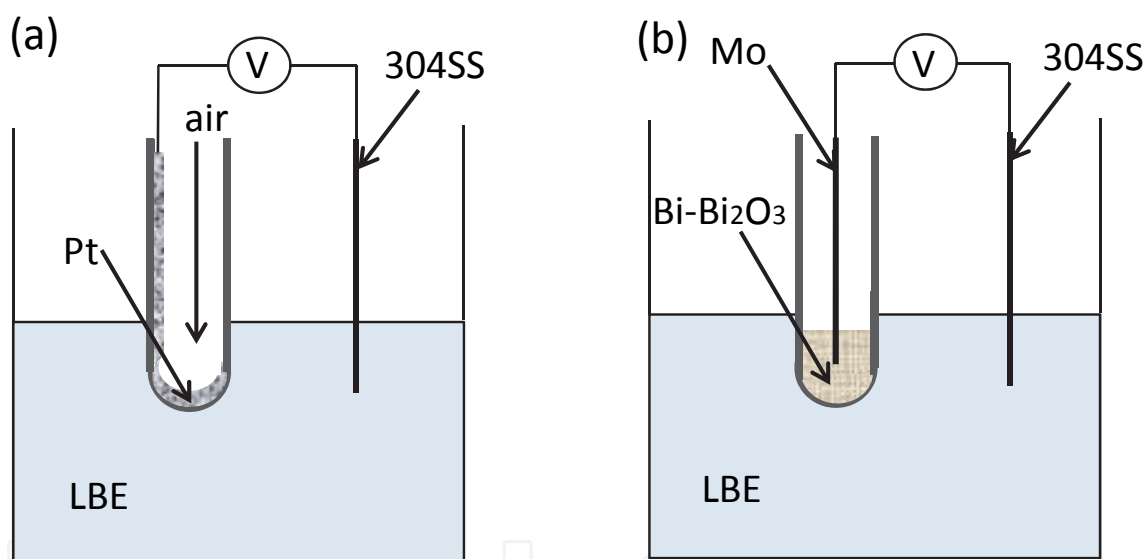


Fig. 3. Schematic diagram of oxygen sensors in liquid LBE: (a) Pt/air reference system and (b) Mo/Bi-Bi₂O₃ reference system.

3. Electromotive force measurement using oxygen sensors

While YSZ sensors with the Pt/gas reference electrode and the Mo/Bi-Bi₂O₃ reference electrode were prepared, the former was mainly used in this study. The Pt/gas reference sensor made by Sukegawa Electric Co., Ltd. was the one-end closed YSZ tube with outer diameter of 15mm and inner diameter of 11mm. The Pt/gas reference system was put inside the YSZ tube. The inner Pt electrode was made by a process of painting Pt-paste inside the YSZ tube and baking it. The porous Pt electrode made through this process has good catalytic activity that enables to measure oxygen concentration at lower temperatures. The fully stabilized zirconia (ZrO₂) with 8 mol% Y₂O₃ produced by Nikkato Corp. was used as a solid electrolyte on account of its good electronic behavior and thermo-mechanical

performance. The Mo/Bi-Bi₂O₃ reference sensor was a sensor using the one-end closed tube of YSZ with the sizes of 8mm in outer diameter, 5mm in inner diameter and 300mm in length. The Mo/Bi-Bi₂O₃ reference electrode was made inside the YSZ tube in our laboratory. The ratio of Bi to Bi₂O₃ was 9:1 in weight. The upper part of the YSZ tube was sealed using alumina cement. This sensor with the Mo/Bi-Bi₂O₃ reference electrode was similar to the Mo/Bi-Bi₂O₃ reference sensor manufactured in other institutes (Courouau et al., 2002b; Konys et al., 2004; Kondo et al., 2006).

The following two methods were employed for calibration of oxygen sensors: (1) comparison between measured EMF values and theoretical ones using two kinds of gases with different oxygen concentrations for the reference electrode and the working electrode, and (2) comparison between measured EMF values and theoretical ones in LBE with the parameter of temperature under the condition close to oxygen saturation in LBE. The advantage of the former method is easiness of preparing the reliable working electrode with the correct oxygen concentration in gas in case of employing a ceramic vessel. The latter method has been often employed as a calibration test in LBE (Konys et al., 2001; Courouau et al., 2002b). An electrometer with high impedance of $10^{14}\Omega$ was used for measurement of the EMF both in gas and in LBE. Schroer et al. conducted calibration tests using not only Pb/Pb-monoxide (PbO) but also Co/Co-monoxide (CoO) and Fe/Fe-oxide equilibria in liquid LBE (Schroer et al., 2011).

3.1 Measurement of oxygen concentration in gas

Figure 4 shows a schematic drawing (a) and appearance (b) of the Pt/gas reference sensor used in measurement of oxygen concentration in gas (Kurata et al., 2010). Platinum paste was painted on the lower part of the outer YSZ surface to measure oxygen concentration in gas. In this test, 10.45%O₂-He gas was used as reference gas and 502ppmO₂-He gas as working gas. The temperature range was 350°C - 600°C and the temperature was kept for about 24h to investigate change of the EMF values at each temperature.

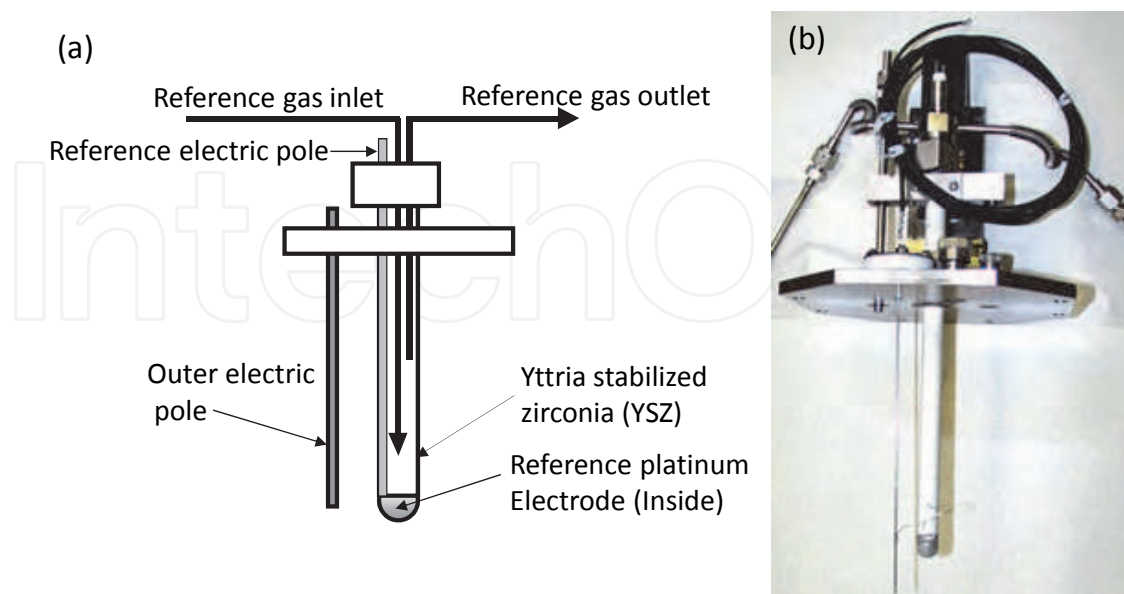


Fig. 4 Schematic drawing (a) of the YSZ oxygen sensor with Pt/gas reference system and appearance(b) of the YSZ oxygen sensor with outer Pt electrode for measurement of oxygen concentration in gas (Kurata et al., 2010).

The relationship between the EMF and temperature is shown in Fig. 5 (Kurata et al., 2010). The theoretical line calculated from Eq. (1) is also drawn in this figure. The EMF values approach the theoretical line of the Nernst relation while it seems to take time to attain the stable outputs below 500°C. This calibration method in gas was often used to investigate correctness of Pt/gas reference sensors.

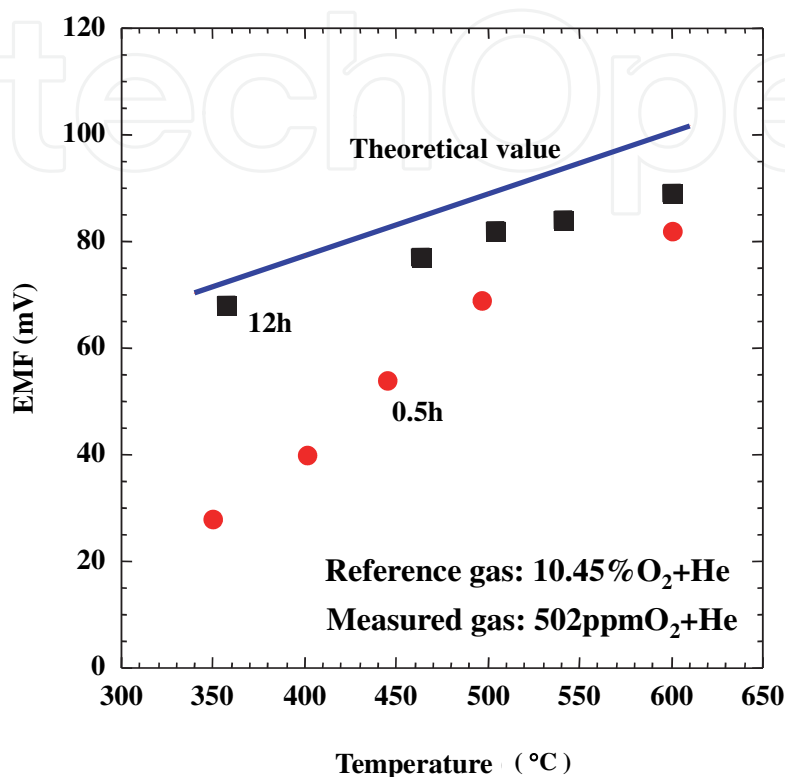


Fig. 5. Relationship between EMF and temperature measured in gas using Pt/gas reference sensor (Kurata et al., 2010).

3.2 Estimation of outputs of the Pt/gas reference sensor in liquid LBE

An apparatus for corrosion tests in LBE (Kurata et al., 2008) was used for the calibration test in LBE. Components contacting liquid LBE were made of quartz. About 7kg of LBE was put into the pot and melted under Ar cover gas with purity of 99.9999% for the calibration test in LBE. The chemical compositions of LBE were 55.60Bi-0.0009Sb-0.0002Cu-0.0001Zn-0.0005Fe-0.0007As-0.0005Cd-0.0001Sn-Bal.Pb(wt%). Initial oxygen content in LBE was usually from 10^{-4} to 10^{-3} wt% in this treatment. Figure 6 depicts a photo showing the Pt/gas reference oxygen sensor under measurement in liquid LBE. A thin PbO film was observed on the surface of the liquid LBE with pure Ar cover gas at 450°C.

Figure 7 shows the relationship between EMF and temperature measured in LBE using Pt/gas reference sensor (Kurata et al., 2010). Air was used as reference gas of the YSZ oxygen sensor. Open circles indicate EMF values measured in oxygen-saturated LBE with pure Ar cover gas. The theoretical line calculated from Eq. (6) for the oxygen-saturated LBE is written with a thick solid line. The measured EMF values are almost on the theoretical line for the oxygen-saturated LBE above 450°C. From the measured EMF value at 550°C, it is estimated that the oxygen concentration in the LBE is about 10^{-3} wt%. The measured EMF

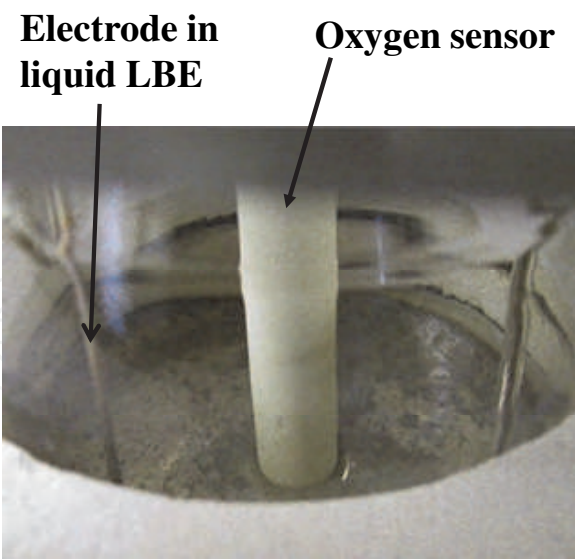


Fig. 6. Photo showing the oxygen sensor under measurement in liquid LBE.

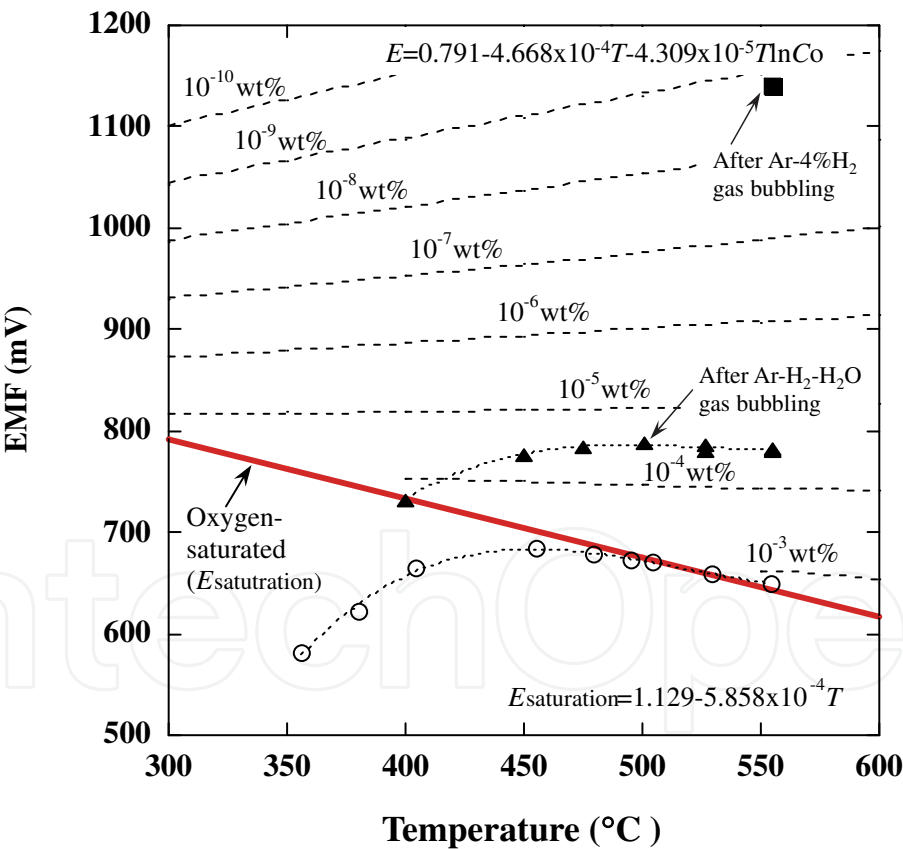


Fig. 7. Relationship between EMF and temperature measured in LBE using Pt/ gas reference sensor (Kurata et al., 2010).

values are much lower than the theoretical line below 400°C. Furthermore, the measured EMF value attained the stable one in LBE above 450°C in short time. From the calibration test using Pb/PbO equilibrium in liquid LBE, it is possible to use the Pt/air reference sensor

above 450°C in liquid LBE. Solid triangles indicate EMF values measured in LBE after Ar-H₂-H₂O gas bubbling. These data were obtained in oxygen-unsaturated LBE. The theoretical lines calculated from Eq. (7) are drawn for the EMF values of oxygen concentrations of 10⁻³wt% to 10⁻¹⁰wt% in LBE. Regarding EMF values measured in LBE after Ar-H₂-H₂O gas bubbling, the slope and the magnitude above 450°C are identical with the expected values for LBE with dissolved oxygen concentration of about 3×10⁻⁵wt%. A solid square shows the EMF value measured in LBE after Ar-4%H₂ gas bubbling. Oxygen concentration of 10⁻⁹wt% in LBE can be measured using the Pt/gas reference sensor. Konys et al. and Schroer et al. also showed validation of oxygen sensors from calibration tests in saturated and unsaturated LBE (Konys et al., 2001; Schroer et al., 2011). On the basis of the results obtained in the present test, it is found that the Pt/air reference sensor enables us to measure oxygen concentration correctly in LBE above 450°C. The appearance of the oxygen sensor after the test in LBE is shown in Fig. 8 (Kurata et al., 2010). Since much LBE adheres to the YSZ surface of the sensor, it is clear that the YSZ surface is wet well with liquid LBE.

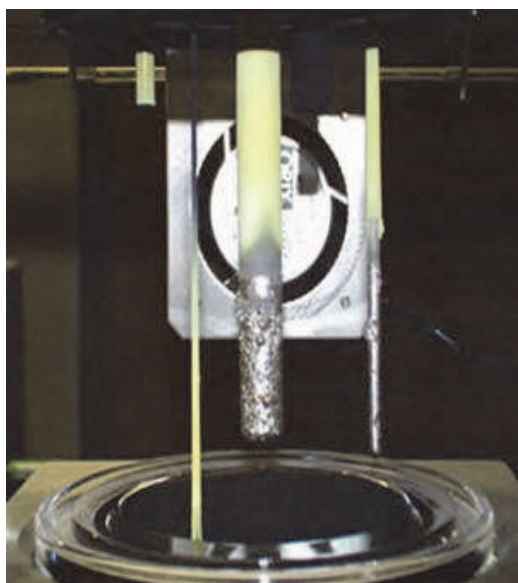


Fig. 8. Appearance of the Pt/gas reference sensor after test in liquid LBE (Kurata et al., 2010).

3.3 Re-activation of oxygen sensor

The Pt/air reference sensor, which exhibited good performance, had been used in LBE for about 6500h. A comparison test was conducted in LBE for the Pt/air reference sensor after long-term use and the Mo/Bi-Bi₂O₃ reference sensor produced in our laboratory. An apparatus shown in Fig. 9 was used for the comparison test of oxygen sensors. The vessel of the apparatus was made of 304SS and outputs from three sensors in liquid LBE could be compared. About 60 kg of LBE was used in the comparison test using 304SS vessel. The procedure similar to that in section 3.2 was employed in the comparison test in liquid LBE. Figure 10 shows the relationship between the EMF and temperature measured in LBE using Pt/air reference and Mo/Bi-Bi₂O₃ reference sensors (Kurata et al., 2010). In the same way as Fig. 7, the theoretical lines calculated from Eq. (6) for the Pt/air reference sensor and from Eq. (8) for the Mo/Bi-Bi₂O₃ reference sensor in the oxygen-saturated LBE are drawn in this figure. It is a surprise that the measured EMF values in LBE with Ar cover gas are much

higher than each theoretical line of oxygen-saturated LBE because oxygen concentration in calibration tests using LBE with Ar cover gas has been constantly in a range of 10^{-4} to 10^{-3} wt%. Therefore, it is necessary to examine whether EMF values measured by both sensors in this test showed correct oxygen concentration or not. Since Ar cover gas does not contain a reducing gas component, it is considered that fresh LBE used in the test contained oxygen of 10^{-4} to 10^{-3} wt%. In the case of the Pt/air reference sensor, the slope of the relationship between the EMF value and temperature is similar to that of the theoretical line above 400°C . Similar trend is also observed in the case of the Mo/Bi-Bi₂O₃ reference sensor above 350°C . These results suggest that oxygen concentration in LBE used in the test was close to saturated oxygen concentration.



Fig. 9. Photo of the comparison apparatus of oxygen sensors. Three sensors can be compared in liquid LBE.

If LBE is oxygen-saturated, it is considered that both sensors exhibited high EMF outputs including somewhat bias voltage. Courouau et al. showed time drift of Mo/metal-metal oxide electrode sensors and presented several hypotheses to explain the cause of the time drift: alteration of the interface of the electrode(working or reference) by oxide deposition, reaction with LBE or the liquid metal reference, or alteration of YSZ affecting eventually the electrode potential (Courouau, 2004; OECD/NEA Handbool, 2007). When the magnitude of the effect on the electrode potential is constant, the alteration can produce constant bias voltage. The comparison tests using the same quartz pot as that in section 3.2 were repeated for the Pt/air reference and Mo/Bi-Bi₂O₃ reference sensors. According to some analyses of results (Kurata et al., 2010), the bias voltage was not always constant although values of bias voltage varied from 200mV to 260mV in repeated calibration tests. Therefore, it is generally difficult to employ the correction method by the constant bias voltage.

Figure 11 depicts appearance of oxygen sensors after measurement in liquid LBE using the comparison apparatus made of 304SS. The black soot of Pb and Bi deposited with LBE on the YSZ surface. There were various surface conditions on the YSZ of the sensors after the comparison tests in LBE. While the YSZ surface was often wet, it was not wet sometimes in particular at low temperatures. Both sensors with Pt/air reference and Mo/Bi-Bi₂O₃ reference electrodes exhibited higher EMF values above 200mV than the theoretical ones above 400°C in all cases after the comparison test.

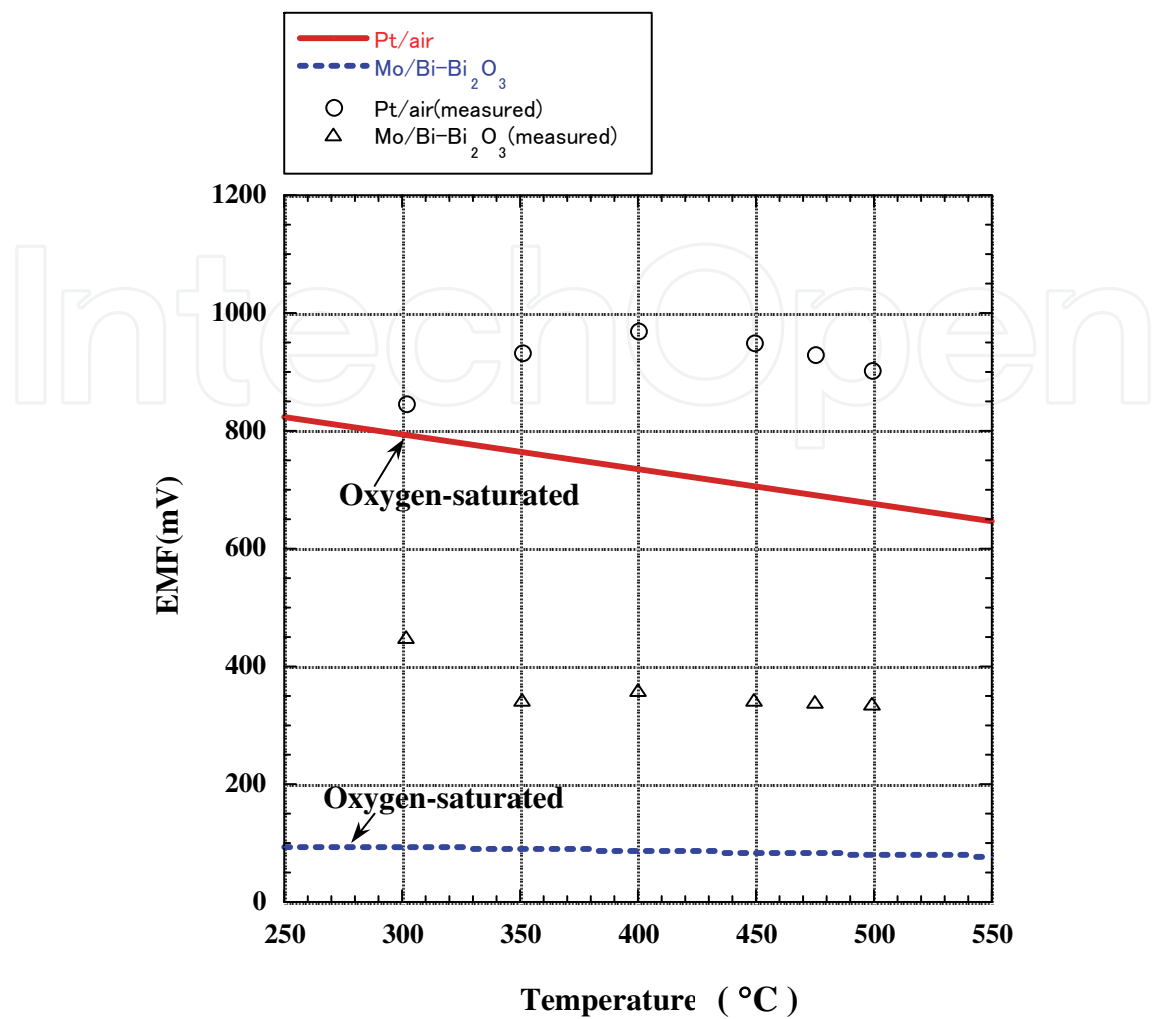


Fig. 10. Relationship between EMF and temperature measured in LBE using Pt/air reference and Mo/Bi-Bi₂O₃ reference sensors (Kurata et al., 2010).

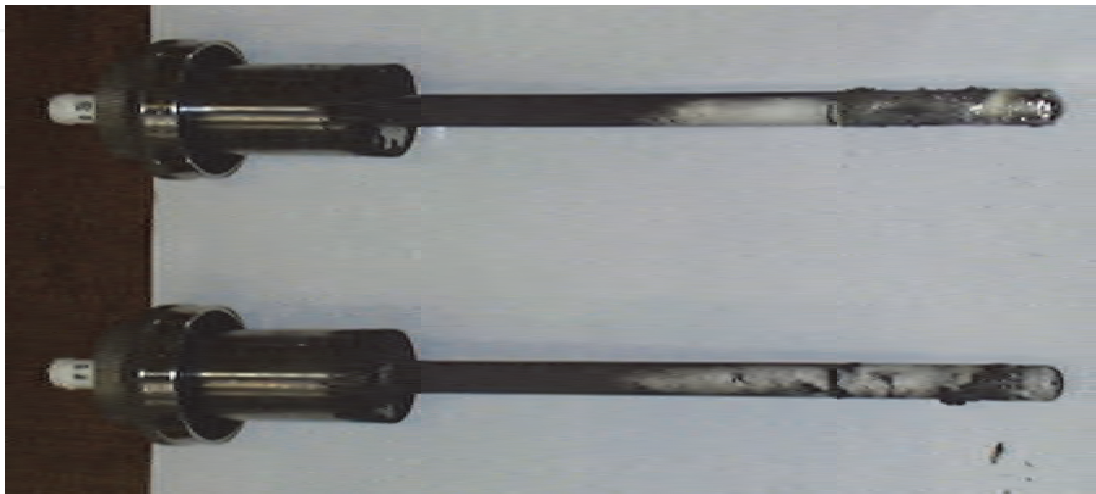


Fig. 11. Appearance of oxygen sensors after measurement in liquid LBE using the comparison apparatus of oxygen sensors.

Investigation of re-activation treatment is one of important research subjets. Some re-activation treatments were attempted for the Pt/gas reference sensor that exhibited incorrect outputs. First of all, the outer surface of the YSZ tube was washed with a nitric acid to remove adherent LBE and black soot. Figure 12 depicts appearance of the Pt/gas reference sensor after cleaning with a nitric acid. Although most of LBE and black soot seem to be removed, there are some black spots left. Figure 13 shows results of the calibration test in liquid LBE using a quartz pot after the cleaning with a nitric acid (Kurata et al., 2010). The Pt/air reference sensor after the washing exhibits higher EMF values by about 220mV than the theoretical line of oxygen-saturated LBE above 450°C. Therefore, it is not capable of recovering the ability of the Pt/gas reference sensor by the method of cleaning with a nitric acid.

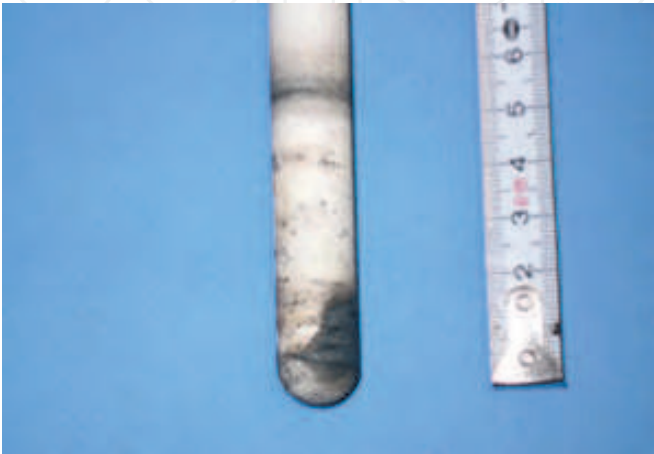


Fig. 12. Photo showing appearance of the Pt/gas reference sensor after cleaning with a nitric acid.

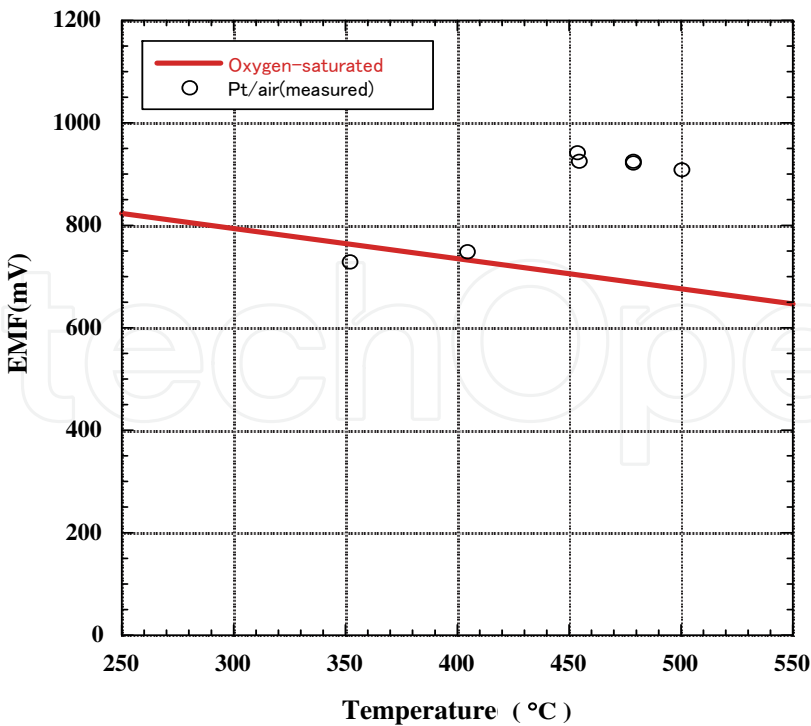


Fig. 13. EMF measurement in LBE using the Pt/gas reference sensor after cleaning with a nitric acid (Kurata et al., 2010).

The Pt-treatment was made on the outer surface of the YSZ next. This treatment is required to measure oxygen concentration in gas and also useful to clean and activate the YSZ surface. Figure 14 shows the relationship between EMF and temperature measured in gas using Pt/gas reference sensors after Pt-treatment (Kurata et al., 2010). The old sensor is the Pt/gas reference one that exhibited incorrect outputs after the comparison tests. The calibration test in gas was also conducted for a new Pt/gas reference sensor. In this calibration test, air was used as reference gas and 504ppmO₂-He gas as working gas. The old Pt/gas reference sensor that exhibited incorrect outputs in LBE indicates the EMF values almost equal to the theoretical ones calculated from Eq. (1) above about 400°C. Furthermore, a new Pt/gas reference sensor exhibits the EMF values almost equal to the theoretical ones above 450°C. The following three causes are considered for the poor condition of the old Pt/gas reference sensor that exhibited incorrect outputs in LBE: (1)failure or degradation of the inner Pt/gas reference system, (2)alteration of YSZ itself and (3)alteration of the outer YSZ surface in contact with liquid LBE. If the cause of the incorrect outputs is failure or degradation of the inner Pt/gas reference system or alteration of YSZ itself, then the old sensor exhibits incorrect outputs in gas. Since the old sensor exhibits correct outputs in gas, the cause of the incorrect outputs seems to be alteration of the outer YSZ surface.

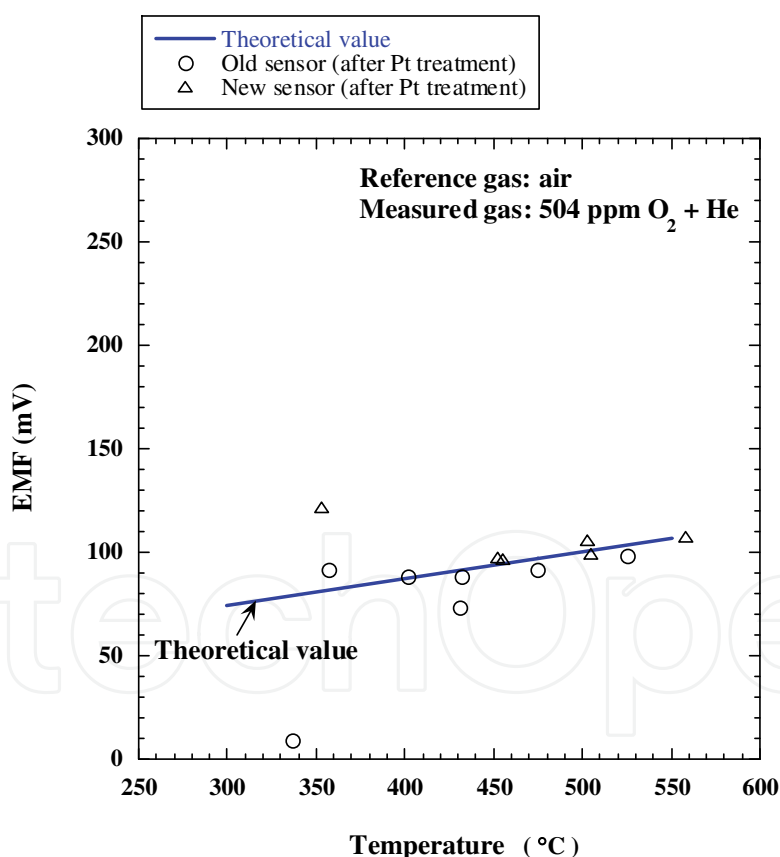


Fig. 14. Relationship between EMF and temperature measured in gas using Pt/gas reference sensors after Pt-treatment (Kurata et al., 2010).

The calibration test in liquid LBE was conducted for both Pt/gas reference sensors after the test in gas. The sensors were soaked into liquid LBE as the state of Pt-treatment on the outer YSZ surface. Results of the calibration test in liquid LBE are shown in Fig.15 (Kurata et al.,

2010). The old sensor after the Pt-treatment exhibits the EMF values almost equal to the theoretical line of oxygen-saturated LBE above 450°C. The new Pt/gas reference sensor after the Pt-treatment also indicates similar behavior. Considering these points into account, the Pt-treatment, which enables us to measure oxygen concentration in gas, seems to play a useful role for measuring oxygen concentration in LBE. As shown in Fig.2, it is essential to continue the interface reaction of Eq. (3) at the outer YSZ surface in contact with liquid LBE in order to measure oxygen concentration correctly using the YSZ electrolyte. The Pt electrode made on the YSZ surface has catalytic characteristics in gas for dissociation reaction of Eq.(2) and enables us to measure oxygen concentration at lower temperatures. The Pt-treatment is composed of painting Pt paste and baking. This treatment produces the porous Pt electrode and clean the YSZ surface. The YSZ interface becomes the activated state due to assistance of the Pt electrode after attaining electrochemical equilibrium under a gas environment. The role of the Pt electrode is a little different in LBE while the Pt electrode is an excellent electrocatalyst in gas. There are two possibilities: improvement of wetting and formation of clean and activated YSZ surface. Dissolution of Pt on YSZ into LBE brings improvement of wetting of the YSZ surface by liquid LBE. Once the YSZ surface is activated in gas by the Pt electrode, the activated state of the YSZ surface will continue in LBE and be useful to promote dissociation reaction at the YSZ surface. The importance of the electrochemical equilibrium of Eq. (3) at the interface between the YSZ and LBE is obvious in measurement of oxygen concentration in liquid LBE using the YSZ electrolyte. When there are highly catalytic electrodes to promote dissociation reaction of Eq. (3) in LBE, it will be possible to conduct measurement of oxygen concentration in LBE with high reliability at low temperatures. Newly developed Ir-C composit and Ru-C composit electrodes, which could operate in a gas environment at temperatures below 300°C due to the excellent catalytic activity (Goto et al., 2001; Sakata et al., 2007), may be useful for the YSZ oxygen sensor with high accuracy and reliability at low temperatures.

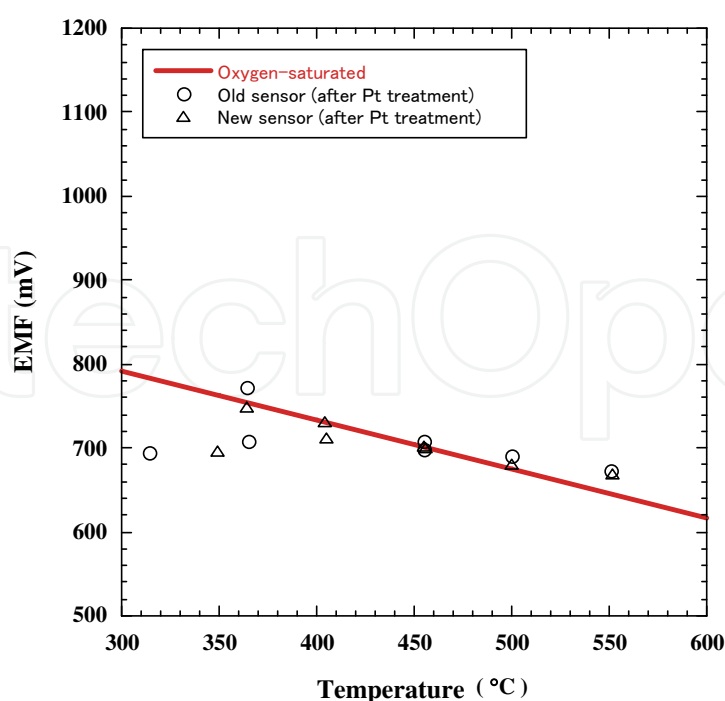


Fig. 15. Relationship between EMF and temperature measured in LBE using Pt/gas reference sensors after Pt-treatment (Kurata et al., 2010).

3.4 Long-term performance of Pt/gas reference sensors

The oxygen sensors with a solid electrolyte of YSZ and a Pt/gas reference electrode have exhibited good performance and been used for a long time in our laboratory to measure oxygen concentration in liquid LBE. Figure 16 shows usage records of the oxygen sensors with the Pt/gas reference electrode. In particular, the sensor-1 was re-activated with Pt-treatment after exhibiting incorrect outputs for some time in liquid LBE. The sensor-1 was used repeatedly for static corrosion tests at 450°C to 550°C through performance tests under gas and liquid LBE environments after re-activation treatment. The cumulative usage time of the sensor-1 attains about 17000h. Controlled oxygen concentration conditions in liquid LBE were 10⁻⁸ to 10⁻³ wt% and a temperature range in measurement using the oxygen sensor was from 350 to 550°C. In addition, the sensor-2 has been used in static corrosion tests of various steels for 5300h. As mentioned above, the oxygen sensor with the Pt/gas reference electrode can be used as a useful sensor to measure oxygen concentration in liquid LBE. Figure 17 depicts variation of electromotive force of the oxygen sensor and the oxygen concentration in liquid LBE during the corrosion test at 550°C for 1000h. The oxygen concentration was controlled using Ar-H₂-H₂O gas flow over liquid LBE during the corrosion test. The H₂/H₂O ratio was changed depending on the oxygen concentration in LBE. The range of H₂/H₂O ratio employed in this corrosion test was from 0.2 to 1.0. As shown in this figure, the oxygen concentration in LBE was controlled in the range of 10⁻⁶ to 10⁻⁴ wt% for 1000h. The accuracy of the oxygen sensor with the Pt/gas reference electrode was checked before the start of each corrosion test through the process that the output of the oxygen sensor at 450°C or 500°C was compared with the theoretical one of oxygen-saturated LBE. This procedure in LBE is a convenient and reliable calibration method of oxygen sensors. The YSZ sensors with the Pt/air reference electrode also showed good durability and reliability for a long time in LBE loop facilities at 550°C (Konys et al., 2004). In static corrosion tests, the YSZ sensors with the Pt/air reference electrode have been used for a long time in our laboratory as the reliable oxygen sensor in liquid LBE.

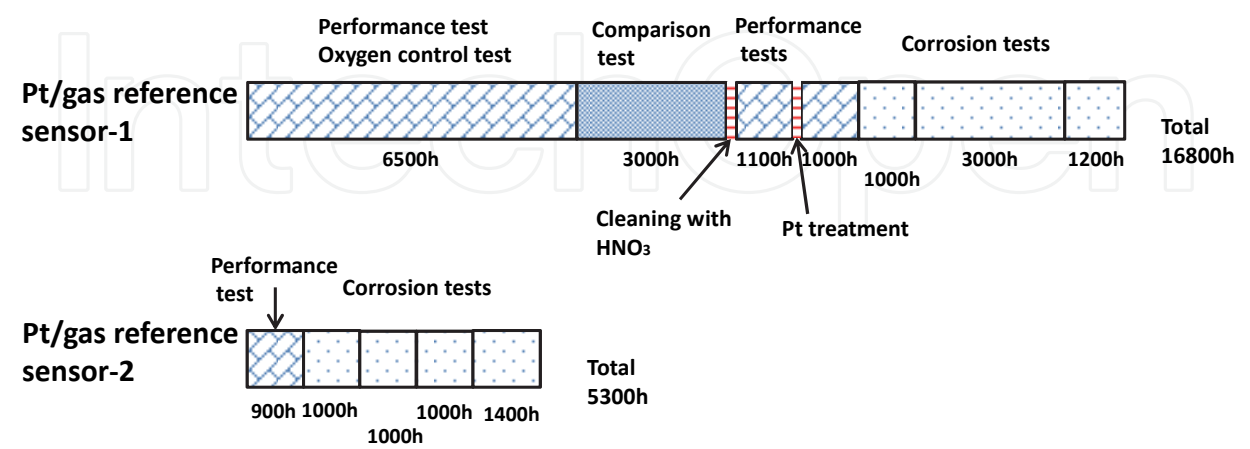


Fig. 16. Usage records of oxygen sensors with Pt/gas reference electrode.

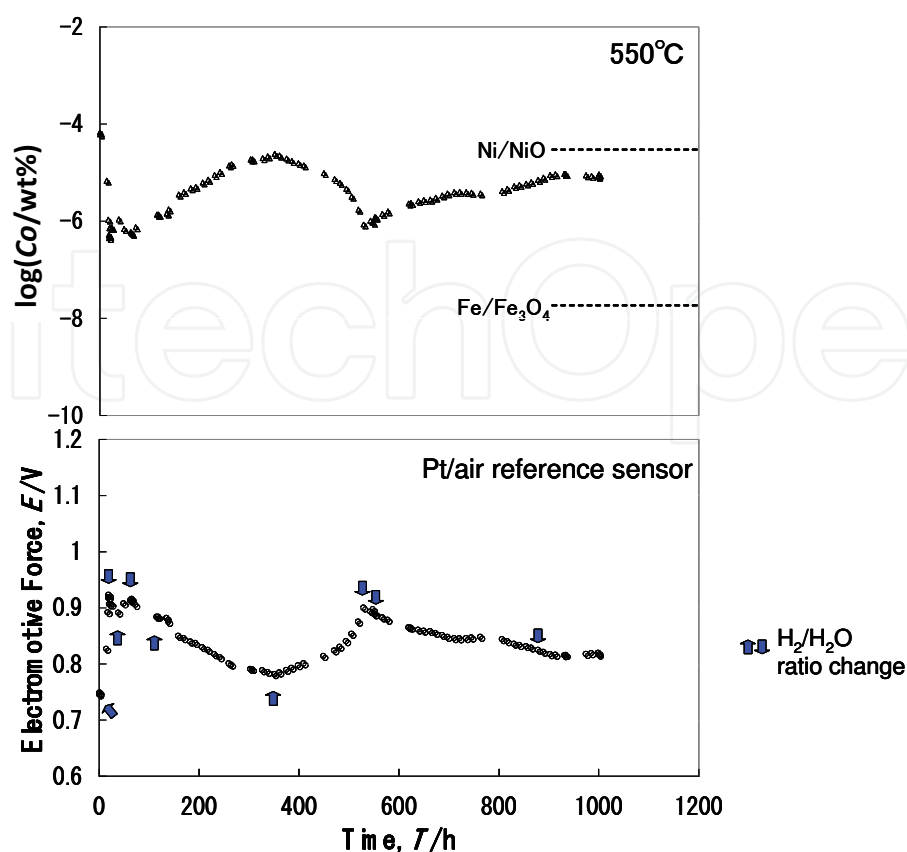


Fig. 17. Oxygen concentration in liquid LBE during the corrosion test at $550^{\circ}C$ for 1000h.

4. Concluding remarks

Electromotive force measurement using oxygen sensors with a solid electrolyte of YSZ and a Pt/gas reference electrode is a useful and reliable means to measure oxygen concentration correctly in liquid LBE online. The accuracy of Pt/gas reference sensors was validated in terms of EMF measurements in gas with known oxygen concentration and in oxygen-saturated LBE. The Pt/gas reference sensors can be certainly used to measure oxygen concentration in liquid LBE at least above $450^{\circ}C$. It occurs that even the YSZ sensor with the Pt/gas reference electrode exhibits incorrect outputs on account of contamination such as deposition of black soot etc. on the outer surface of the YSZ. It is possible to re-activate the YSZ sensor, which exhibited incorrect outputs, by means of Pt-treatment on the outer YSZ surface. The attainment of the electrochemical equilibrium at the interface between YSZ and LBE is important in EMF measurement using the YSZ sensor to estimate oxygen concentration in liquid LBE. The YSZ sensors with the Pt/gas reference electrode have been used for a long time as a reliable oxygen sensor to monitor oxygen concentration in liquid LBE online.

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