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ScienceDirect

Energy Procedia 131 (2017) 420–427

Energy Procedia

www.elsevier.com/locate/procedia

5th International Symposium on Innovative Nuclear Energy Systems, INES-5, 31 October – 2 November, 2016, Ookayama Campus, Tokyo Institute of Technology, JAPAN

Electrochemical impedance analysis on solid electrolyte oxygen sensor with gas and liquid reference electrodes for liquid LBE

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Abstract

The ionic conductivity of solid electrolyte may insufficient, and the sensor output signal will deviate from the theoretical one in low temperature. The performance of oxygen sensor with Ag/air reference electrode (RE) and liquid Bi/Bi_2O_3 RE was tested in low-temperature LBE at 300°– 450°C and the charge transfer reactions impedance at the electrode-electrolyte interface was analyzed by electrochemical impedance analysis (EIS). After steady state condition, both of the sensors performed well and can be used at 300°– 450°C. Bi/Bi_2O_3 RE has lower impedance than Ag/air RE. Therefore, the response time of the oxygen sensor with Bi/Bi_2O_3 RE is faster than the oxygen sensor with Ag/air RE in the low-temperature region.

Keywords: Solid Electrolyte Sensor; Electrochemical Impedance Spectroscopy; Lead-bismuth Eutectic; Accelerator Driven System

1. Introduction

Measurement of oxygen concentration in liquid lead-alloy is necessary to control the oxygen concentration. The oxygen sensor has been proposed as the instrument to measure the oxygen content for the oxygen control in the lead-alloy fast reactor (LFR) and Accelerator Driven System (ADS) [1]. The studies of oxygen sensor for use in liquid lead-

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10.1016/j.egypro.2017.09.472

alloy at high temperature have been performed [2,3]. However, the range of working temperature of the coolant is 200 - 500°C for the ADS reactor [4]. The ionic conductivity of solid electrolyte may insufficient, and charge-transfer reaction rate at electrode-electrolyte interface is low at low temperature. The response time of oxygen sensor is influenced by the oxygen ionic conductivity of solid electrolyte and charge-transfer reaction rate at reference electrode-electrolyte interface [5]:

$$\frac{1}{2} O_{2(gas)} + 2e^{-}_{(electrode)} = O^{2-}_{(electrolyte)} \quad (1)$$

Therefore, the sensor output signal may deviate from the theoretical one derived from Nernst equation at low temperature. It had been reported that solid electrolyte YSZ material can be used down to 300°C in LBE [6]. Thus, the minimum temperature that we investigated start from 300°C.

From the previous study, Courouau et al. [7] had accuracy of 40% at the condition 280°-550°C, 10^{-14} -10^{-3}wt%, through the comparison between experimental results and theoretical formulation. Courouau [8] pointed out that a lower operating temperature than 350°C is possible but with a lower accuracy. Wu et al. [9] just proposed calibration method of YSZ oxygen sensor by varying hydrogen to water steam ratio in liquid LBE at temperature from 300°C to 450°C. They [7-9] only used Bi/Bi_2O_3 reference electrode (RE). But the other type of RE should be tested to see the accuracy. Since the performance of Ag/air RE was good in our result, our new proposal is to use Ag/air RE in liquid LBE at temperature below 450°C. It is necessary to find optimum material for the selection of RE of oxygen sensor at the low-temperature region lower than 450°C. The originality of the present study is to find the optimum material for the selection of RE of oxygen sensor at the low-temperature from 350°C to 450°C.

Another originality of the present study is to use electrochemical impedance spectroscopy (EIS) method to find the optimum material as mentioned above. The EIS method has been used to judge the condition of solid electrolyte and environment condition, such as short circuit and PbO deposited on the surface of electrolyte [1]. However, the EIS method has additional ability to analyze the charge transfer reactions impedance at electrode-electrolyte interface to determine the optimum material for RE of oxygen sensor [10]. The optimum material of RE should have lower charge transfer reaction impedance by means lower charge transfer resistance. This paper is the first paper to apply EIS method to determine the optimum material by analyse charge transfer reaction impedance.

The purpose of this study is to investigate the cell potential (*E*) of oxygen sensors with Ag/air RE and Bi/Bi_2O_3 RE in liquid LBE at temperature 300 - 450°C as preliminary check and to analyse the impedance of oxygen sensor with Ag/air RE and Bi/Bi_2O_3 RE in liquid LBE at temperature 350 and 450°C to determine the optimum material of RE.

Nomenclature

A	Effective contact area between eletrode and electrolyte (cm^2)
C	Capacitance (f)
C_{dl}	Double layer capacitance (f)
C_O	Oxygen concentration in LBE (wt%)
$C_{O,s}$	Oxygen concentration of oxygen saturated condition in LBE (wt%)
F	Faraday constant, =96485 (C/mol)
$G^{EX}_{O,LBE}$	Excess molar Gibbs free energy of LBE (J/mol)
l	Thickness of solid electrolyte (cm)
PO_2^{ref}	Oxygen partial pressure in reference electrode (bar)
PO_2^{wor}	Oxygen partial pressure in working electrode (bar)
R	Gas constant, =8.314 (J/K.mol)
R_{el}	Resistance of solid electrolyte (Ω)
R_{ct}	Charge-tranfer reaction resistance (Ω.cm^2)
T	Absolute temperature (K)
$\Delta G^0_{Bi_2O_3}$	Gibbs free energy for formation of Bi_2O_3 (J/mol)
σ	Conductivity of solid electrolyte (S/cm)