Development of Electrochemical Oxygen Sensor for High Temperature Sodium Environment Application

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1. Introduction

Sodium is one of candidate coolants for Advanced Fast Reactor that utilizes LWR spent fuels. With that, the compatibility of cladding and structural materials with sodium has to be carefully investigated.

It is well known that sodium could promote corrosion in two ways. One is corrosion produced by dissolution of alloy elements into sodium, and the other is corrosion produced through a chemical reaction with impurities (especially oxygen) in sodium environment [1]. With later consideration, the concentration of dissolved oxygen in sodium has to be monitored and controlled at the operating condition.

An electrochemical sensor for measuring oxygen concentration in liquid sodium that is based on a GDC (Gadolinium Doped Ceria) electrolyte has been developed in this study.

2. Experiments

Oxygen ion conducting solid oxide electrolytes are well known and their properties have been comprehensively reviewed [2-4]. The most common commercially available electrolyte materials are those based on zirconia (ZrO_2) and thoria (ThO_2). However, zirconia is not suitable in sodium environment due to the reaction compound, Na_2ZrO_3, which is easily formed and more stable than zirconia.

While thoria is very stable materials in sodium environment, few disadvantages drive for alternatives. The sintering temperature of thoria is 2000°C and it is expensive materials [5].

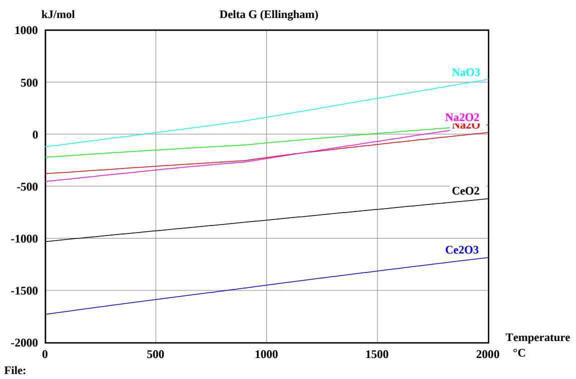

Fig. 1. Gibbs free energy changes of Na-Ce-O system (by HSC 6.0).

In this study, ceria based electrolyte are first introduced and studied as candidate materials for electrochemical membrane of oxygen concentration sensor in sodium environment.

As seen in Fig. 1, the compatibility of ceria (CeO_2) at elevated temperature sodium is very stable. Furthermore, oxygen vacancies can be introduced by substituting a fraction of the ceria with trivalent oxides, such as Y_2O_3, Sm_2O_3 and Gd_2O_3 to increase the ionic conductivity of ceria [6]. Among those oxides, gadolinia (Gd_2O_3) was selected and doped into ceria due to its high ionic conductivity as shown in Table I. Gadolinia doped ceria powder has been sintered at 1400°C for 1 hour and its microstructure is shown in Fig. 2. When gadolinia doped into ceria, the electronic conduction of GDC (gadolinia doped ceria) is known to change from n-type to p-type with increasing oxygen partial pressure in liquid sodium [7]. A major drawback is the distinctly higher electronic conductivity of ceria at low partial pressure of oxygen. However, at temperature below 800°C, the electronic conductivity seems to be low enough to make possible its use as solid electrolyte over the interesting oxygen activity range between $\alpha_{O2}=1$ and $\alpha_{O2}=10^{-18}$ [8].

2.1 Oxygen Sensor Design

Oxygen sensor mainly consists of electrolyte, metal housing and reference electrodes as shown in Fig. 3. And the joining method between electrolyte and metal housing is also important process due to their different coefficient of thermal expansion [9].

$15CaO-10Al_2O_3-53BaO-22B_2O_3$ glass bonding materials were used to make leak-tight bonding between GDC electrolyte and Fe-48Ni alloy that has similar thermal expansion with GDC.

As reference electrode, In/In_2O_3 are selected in this study, the electrode could generate reproducible output signal [10].

Table I. Basic property of ceramic materials [2-4]

	CTE (ppm/°C)	IC (S/cm)
GDC-10	13.4	-1.2
SDC-15	12.7	-1.3
YDC-10	14.5	-3.7
YSZ-10	10.8	-2.25

*CTE: Coefficient of Thermal Expansion
*IC: Ion Conductivity at 700°C
*GDC: Gadolinia Doped Ceria
*SDC: Samaria Doped Ceria
*YDC: Yttria Doped Ceria *YSZ: Yttria Stabilized Zirconia

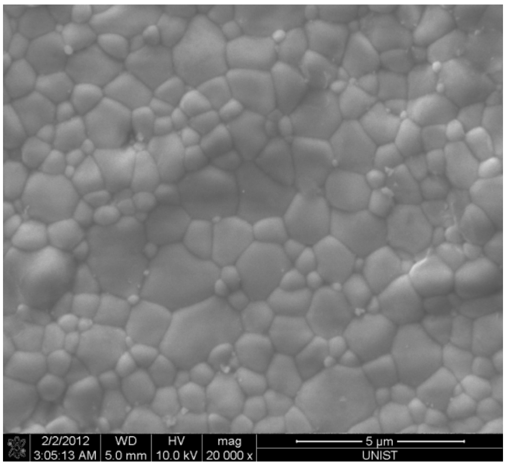

Fig. 2. Microstructure of GDC10 (Gadolinium Doped Ceria) electrolyte tube (x20000).

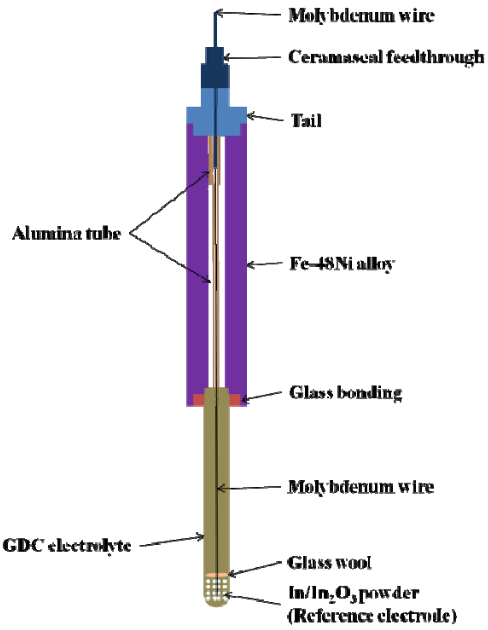

Fig. 3. The basic features of oxygen sensor.

When sodium and indium oxidizes, the Gibbs free energy changes are shown in equations (1) and (2), respectively. In this system, oxygen sensor's output signal is shown in equation (3) [10].

$$\Delta G_f^0(2Na_2O) = -844791 + 288.3T(K)\ J/mol\ O_2 \quad (1)$$

$$\Delta G_f^0(In_2O_3) = -611512 + 210.4T(K)\ J/mol\ O_2 \quad (2)$$

$$E = 0.29625 \pm 0.00809 + \frac{125.86}{T_{ct}(K)} \quad (3)$$

Where, T_{ct} is the temperature of cold trap in sodium loop.

2.2 Sodium loop system

Sodium loop system is developed to measure oxygen concentration in this study.

Total 9.8kg of sodium is used and it flows with 2m/s through 3/8" stainless steel tube by electromagnetic pump. Oxygen concentration will be controlled by the temperature control in cold trap. The target oxygen concentration in sodium is below 10wppm. And oxygen measurement will be conducted in corrosion cell with compatibility test of UCFR candidate materials.

3. Summary

Gadolinia doped ceria (GDC) electrolyte is used as a part of oxygen concentration sensor due to its high oxygen ionic conductivity and stability in sodium environment. And the joining process between electrolyte (GDC) and metal housing (Fe-48Ni) have finished. The remaining process is to make complete electrochemical cell as shown in Fig. 3. And oxygen concentration will be measured and calibrated in sodium loop system. It would be also the main work in this study.

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