Solid State Ionics 240 (2013) 34–40

Contents lists available at SciVerse ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Lifetime of the internal reference oxygen sensor

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ARTICLE INFO

Article history:
Received 28 July 2012
Received in revised form 23 January 2013
Accepted 12 March 2013
Available online 12 April 2013

Keywords:
Electronic conduction
Doped zirconia
Depletion period
Oxygen sensor
Internal reference

ABSTRACT

The internal reference oxygen sensor (IROS) based on a binary mixture of metal and its stoichiometric oxide is subject to leaks that result in consumption of the binary mixture. An IROS loses the functionality when the binary mixture is exhausted. Among the possible leak sources the electronic leak of electrolyte is usually unavoidable. Thus, evaluation of the electronic conduction of electrolyte is useful for lifetime estimation. In this study the electronic conduction of 8 mol% yttria doped zirconia (8YSZ) that is typically used as the electrolyte for solid oxide cells including the IROSes is evaluated, and the depletion period of an IROS based on the binary mixture of Ni/NiO is discussed. The theoretical prediction of the depletion period is verified by experimental results over more than 6600 h. Figures that may be used to predict the depletion period are provided for practical cell design. The electronic conduction of electrolyte can be minimized to make the depletion period of an IROS satisfy the target application up to duration of years.

1. Introduction

Potentiometric oxygen sensors work by the Nernst equation and pO_2 is determined from the cell voltage between the reference electrode and the sensing electrode [1]. To determine the pO_2 at the sensing electrode the pO_2 at the reference electrode must be known. Usually the reference pO_2 is provided by conveying air to the reference electrode, which, however, is sometimes difficult or impossible, especially in the large and complex industrial equipments [1,2]. An internal reference oxygen sensor, if available and reliable, is favored since it is free of the reference air. The reference pO_2 in an internal reference oxygen sensor can be established by a pump-gauge design [2–5] or by a binary mixture of metal and its stoichiometric oxide [1,6–13]. The latter cells prevail in the R&D activities as the pump-gauge cells have a complex structure and their accuracy and stability are not satisfactory [2–5]. In this study the internal reference oxygen sensor (IROS) refers exclusively to the cell based on a binary mixture.

Leaks have been challenges for developing commercializable IROSes. The leak sources were discussed previously by Kaneko et al. [5]. Fig. 1 illustrates the structure of an IROS and indicates possible leak sources. Leak 1 is due to electronic conduction of the electrolyte. Though a potentiometric oxygen sensor usually uses an oxide with high ionic conductivity, i.e. doped zirconia, as the electrolyte, a tiny but finite electronic conductivity of the electrolyte is always encountered. Leak 2 is caused by oxygen molecules that permeate through a non hermetic seal or a non dense electrolyte. Leak 3, the electrochemical leak, results from inappropriately fabricated metallic contacts that are used for sealing and/or electrical connecting the internal reference electrode (IRE). In some cases metallic foils [5] such as gold foils or a coating of Au/Ag deposited by pulsed laser [9] are used to cover the internal reference electrode for sealing or electrical connection. If these metallic contacts/coating form a percolating connection for electrons between the internal reference electrode and the sections of the electrolyte exposed to the external atmosphere, they will serve as a passage of low resistance for electron transfer. The triple phase boundary (TPB) [14] is thus formed inside and outside the seal and oxygen molecules can then be reduced at the side of high pO_2 and be evolved at the side of low pO_2.

The leaks allow oxygen transport into or out of the internal reference electrode. One of the functional components of the binary mixture is consequently consumed, which eventually depletes the binary mixture and makes the IROS lose the functionality. Therefore leaks should be avoided as much as possible. Leak 2, the oxygen molecule leak, and leak 3, the electrochemical leak, can be avoided if the cell structure is properly designed and cell fabrication is carried out carefully, upon sufficient fabrication expertise. For example, a hermetic seal and a dense electrolyte have been reported by several studies [6,7,9,10]. Formation of the TPB is prerequisite for the electrochemical leak to take place. If all metal contacts to the IRE are carefully fabricated and have no connection to the electrolyte on its course out of the seal, the electrochemical leak will be avoided. Contrary to leaks 2 and 3, leak 1, the electronic leak of electrolyte cannot be eliminated since it is an intrinsic characteristic of the oxide serving as the electrolyte. Therefore it is of importance for practical purposes to evaluate the rate of the electronic leak of the electrolyte and find out the means to minimize its effects on the depletion period in order to meet application requirements.

According to the Gibbs phase rule the equilibrium pO_2 of a binary mixture is fixed at a given temperature, meaning that the theoretical voltage

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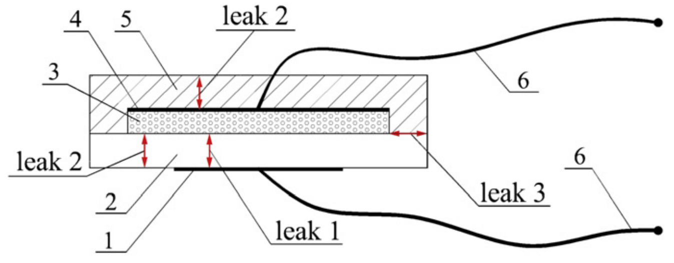
http://dx.doi.org/10.1016/j.ssi.2013.03.025



1: sensing electrode 2: electrolyte
3: internal reference electrode (IRE)
4: metalic contacts/coating over the IRE
5: seal 6: metal lead

Fig. 1. Structure of an IROS and possible leak sources. Leak 1: electronic leak of the electrolyte. Leak 2: oxygen molecule leak due to a non hermetic seal or a non dense electrolyte. Leak 3: electrochemical leak caused by inappropriately fabricated metallic contacts.

of an IROS can be determined at a known temperature and should be maintained once the binary mixture is present at a constant temperature. However, most of the published responses of IROSes deviate from the nominal value to a noticeable extent and tend to decrease in a short period, i.e. 100 h [1,6–13]. In a recent publication [10] IROSes based on the binary mixtures including Ni/NiO, Pd/PdO and Ru/RuO_2 were demonstrated but the voltage of the cells was subject to decrease over time, i.e. in a period of tens of hours, which was ascribed solely to the electronic leak of the electrolyte. However, there could be other major leak sources instead of the electronic leak of the electrolyte accounting for the cell voltage decrease, as we have witnessed a stable service of more than 5500 h on our IROS based on the binary mixture of Ni/NiO [7]. Nevertheless, it is necessary to investigate theoretically the depletion period of an IROS since it plays a key role in determining the commercial potential of the technology. The subjects of this study thus are to give a quantitative evaluation on the electronic conduction of electrolyte and to provide tools that may be used to "design" the electronic leak of an electrolyte in order to satisfy the application requirements.

2. Theory

The structure of an IROS is noted as IRE(O_2, p_R)|Elyt|SE(O_2, p_S) where Elyt denotes the electrolyte, p_R and p_S, indicate the pO_2 at the interfaces of IRE/Elyt and SE/Elyt, respectively. The concentrations of holes and electrons of the electrolyte normally are dependent on pO_2, i.e. the hole concentration and electron concentration of 8 mol% yttria doped zirconia (8YSZ) are proportional to pO_2 to the power of ¼ and −¼, respectively [17]. If the pO_2 at the interface SE/Elyt is significantly different from that at the interface IRE/Elyt, which is common in practice, differences in the concentration, and therefore in the chemical potential of electrons and holes between the two interfaces will be established. As a result, holes transfer in one direction while electrons transfer oppositely. To avoid charge accumulation oxide ions transfer simultaneously. The analysis below is performed with the assumptions that the internal reference electrode consists of Ni/NiO and electrolyte is made from 8YSZ, both of which are representative in practice [1,7,8,10,15,16].

Fig. 2 illustrates the transfer of charge carriers through the electrolyte with the assumption that the pO_2 at the interface IRE/Elyt is much less than the pO_2 at the interface SE/Elyt, i.e. $p_R \ll p_S$. This assumption is usually fulfilled in reality as the equilibrium pO_2 of a binary mixture of a non noble metal and its oxide is generally very low, e.g. the equilibrium pO_2 of Ni/NiO is 5.5×10^{-17} bar at 700 °C. Under this condition electrons transfer from the interface IRE/Elyt to the interface SE/Elyt, holes transfer in an opposite direction, from the interface SE/Elyt to the interface IRE/Elyt, and oxide ions transfer in the same direction as holes. As a result the metallic Ni in the IRE is consumed by the permeating oxide ions.

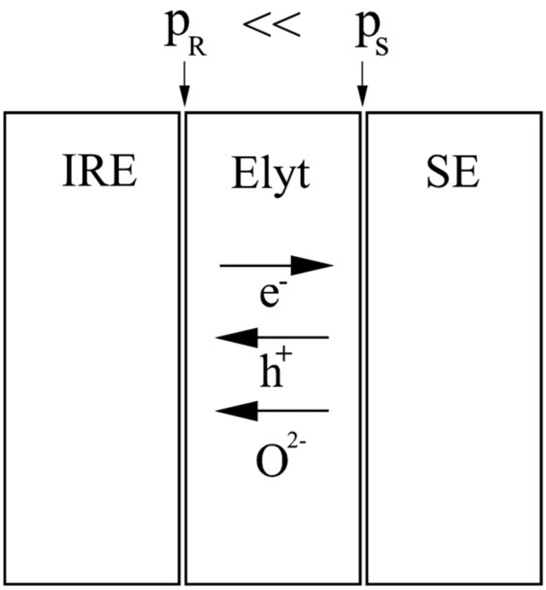


Fig. 2. Transfer of electrons, holes and oxide ions in the electrolyte of an IROS under a significant difference in pO_2 between the interfaces IRE/Elyt and SE/Elyt. The pO_2 at the interface IRE/Elyt is assumed to be much less than the pO_2 at the interface SE/Elyt.

In the transfer processes of the charge carriers, the current density of individual charge carrier is proportional to the gradient of the electrochemical potential [18–20]:

$$i_k = -\frac{\sigma_k}{z_k F}\nabla\overline{\mu}_k, \quad k = i, e, h \tag{1}$$

where $\sigma, \overline{\mu}$ and z indicate conductivity, electrochemical potential and charge number, respectively, and the suffix k can be i, e and h, corresponding to oxide ions (i), electrons (e) and holes (h). The electrochemical potential of charge carrier k, $\overline{\mu}_k$, is the sum of a chemical part and an electrical part [20,21]:

$$\overline{\mu}_k = \mu_k + z_k F\phi \tag{2}$$

where ϕ is the Galvani potential and μ_k is the chemical potential of charge carrier k. Assume two equilibria of defect reaction within the electrolyte [20,21]:

$$\frac{1}{2}O_2 + 2e^- \leftrightharpoons O^{2-} \tag{3}$$

$$e^- + h^+ \leftrightharpoons nil \tag{4}$$

One obtains the conditions of equilibrium in terms of electrochemical potentials:

$$\nabla\overline{\mu}_e = \frac{1}{2}\nabla\overline{\mu}_i - \frac{1}{4}\nabla\mu_{O_2} \tag{5}$$

$$\nabla\overline{\mu}_e = -\nabla\overline{\mu}_h \tag{6}$$

The leak current is carried by electrons and holes, meaning:

$$i_{eh} = i_e + i_h \tag{7}$$

where i_{eh} is the leak current density and is compensated by the current density of oxide ions [20,21]:

$$i_{eh} = -i_i \tag{8}$$