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## Solid State Ionics

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# Determination of oxygen surface exchange constant of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ coated with $Ce_{0.9}Gd_{0.1}O_{1.95}$ by isotope exchange technique



SOLID STATE IONIC

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#### ARTICLE INFO

Article history: Received 20 August 2015 Received in revised form 7 December 2015 Accepted 7 December 2015 Available online 29 December 2015

*Keywords:* Surface oxygen exchange kinetics Isotope exchange Secondary ion mass spectrometry

#### ABSTRACT

The surface oxygen exchange coefficient ( $k^*$ ) of LaNi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>3-6</sub> (LNF) coated with porous Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (GDC) was determined by the isotope exchange technique. The LNF coated with GDC was subjected to isotope exchange treatment where <sup>16</sup>O<sub>2</sub> was abruptly changed into <sup>18</sup>O<sub>2</sub> at a range temperature of 873-1073 K under 10<sup>-1</sup> and 10<sup>-2</sup> bar of the oxygen partial pressure ( $p(O_2)$ ). The line-scanning mode of secondary ion mass spectrometry was used to determine the surface oxygen exchange of the LNF coated with GDC. The  $k^*$  of LNF coated with GDC is enhanced compared to that of the bare LNF due to the formation of triple phase boundary between LNF, GDC, and gas phase of oxygen. The role of GDC is enhancing the incorporation process of the oxygen dissociated at the LNF surface. The adsorption and dissociation of oxygen takes place at LNF surface and incorporated into GDC porous.

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#### 1. Introduction

Mixed ionic and electronic conductor (MIEC) type materials have been studied for a few decades due to the ability to reduce oxygen at the surface [1,2]. The MIEC gives a chance to improve the performance of the solid oxide fuel cell (SOFC). Several MIECs such as  $(La,Sr)CoO_3$ (LSC) and  $(La,Sr)(Co,Fe)O_3$  (LSCF) have been utilized as the state the art cathode of SOFC. On the other hand,  $La(Ni,Fe)O_3$  electrode is relatively a new cathode material which has been studied in the last decade and shows promising performance [3–5].

LaNi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>3- $\delta$ </sub> (LNF) shows superior electronic conductivity and ionic conductivity. Nishi et al. mentioned that LNF shows a comparable value on the ionic conductivity to LSCF [6]. In addition, they suggested that the oxygen surface exchange kinetics ( $k^*$ ) of LNF is relatively high among MIEC electrode. In order to enhance the electrochemical performance, the MIEC is often mixed with ionic conducting oxide such as yttria-stabilized zirconia (YSZ) or doped ceria based electrolyte [7–9]. The performance of the composite electrode is enhanced drastically compared to single phase electrode.

In our preceding work, composite electrode of LNF and Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (GDC) has been studied and showed drastic enhancement on the electrochemical performance [10]. Such a large enhancement on MIEC which has relatively high ionic conductivity is difficult to be understood by a simple explanation of the extended contact area between electronic and ionic conducting oxide. Another factor may

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The study by Hong et al. on the surface reaction of LSCF coated with samaria-doped ceria (SDC) gives another way to understand the reaction mechanism of oxygen reduction process in a composite electrode [11]. They found that the  $k^*$  of LSCF enhances drastically with the existence of SDC particles on the surface [11]. This result suggests that the enhanced was not the ionic conduction but the surface reaction rate in a porous composite electrode.

In this study, an LNF bulk sample, which is coated by GDC has been investigated by isotope exchange technique to determine the  $k^*$  at controlled temperature and  $p(O_2)$ . Isotope exchange technique is one of powerful techniques to determine the surface exchange kinetics [12, 13]. The analysis by secondary ion mass spectrometry determines the diffusion profile of  ${}^{18}O/{}^{16}O$  inside the bulk sample. By combine the isotope exchange and secondary ion mass spectrometry, the  $k^*$  of LNF coated with GDC has been determined and compared to bare LNF. In this study, the enhancement of the surface exchange kinetics will be discussed in order to determine the reaction pathways of the oxygen reduction process.

#### 2. Experimental

#### 2.1. Sample preparation

A LaNi<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>3- $\delta}$ </sub> (LNF) powder was prepared by Pechini method. The powder was calcined at 1073 K for 6 h to obtain a single phase, which was confirmed by XRD (M18X CE, Mac Science). The LNF powder was pulverized and then pressed into a pellet at 200 MPa. The pressed



sample was sintered at 1523 K for 6 h and cut into a rectangular shape of  $2 \text{ mm} \times 2 \text{ mm} \times 5 \text{ mm}$ . The sample was polished by diamond suspension to get a fine surface prior to GDC deposition.

A Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> (GDC) powder was provided by a commercial powder (Shin-Etsu Rare Earth, Shin-Etsu Chemical). The GDC was mixed with ethyl cellulose (Wako Pure Chemical Industries, Ltd., Japan) and organic solvent, TMS-1 (Tanaka Kikinzoku Co., Japan), to get slurry of GDC. The GDC was deposited onto LNF bulk surface by screen printing method. The samples of LNF coated with GDC were sintered at 1273 K. After sintering, the samples were pre-annealed for the 3 h prior to the isotope exchange treatment. The average particle size of GDC particle which coated to LNF surface was determined by scanning electron microscopy (SEM, JEOL JSM-700 1F). The average particle size of GDC is around 1  $\mu$ m as shown in Fig. 1.

#### 2.2. Isotope exchange and secondary ion mass spectrometry

The sample was placed into the alumina chamber, which was placed into glass for isotope exchange treatment. The thermocouple (Pt/Pt-13%Rh) was attached to the alumina chamber to monitor the temperature. The sample was heated up to the constant temperature at <sup>16</sup>O<sub>2</sub> for 30 min before the gas was abruptly changed to the isotope enriched one (<sup>18</sup>O<sub>2</sub>, 99% purity). The exchange times were varied depending on the temperature and  $p(O_2)$  condition. For 873 K under  $10^{-2}$  bar, the exchange time was around 30 min after subjected into <sup>16</sup>O<sub>2</sub>. In the other case, at 1073 K under  $10^{-2}$  bar, the exchange time was around 10 min after <sup>16</sup>O<sub>2</sub> abruptly changed into <sup>18</sup>O<sub>2</sub>. After that, the sample was quenched to the room temperature in 60 s.

The quenched samples after the isotope exchange were used for SIMS measurement. For LNF coated with GDC sample, the GDC porous layer was removed from LNF prior to SIMS measurement. The sample was put into an acetone in order to remove the GDC porous layer from the surface of the LNF bulk. The sample was cut to get the cross section surface and then polished to get a fine surface. The secondary ion mass spectrometer (SIMS, CAMECA IMS-7F) was utilized to determine the diffusion profile of the samples. The Cs<sup>+</sup> (15 keV) was used as a primary ion beam of the SIMS. The line scanning mode was used where the points of measurement were taken from the edge of the sample up to 500  $\mu$ m with a primary ion beam of 0.5 nA. The negative ion signal of <sup>16</sup>O<sup>-</sup> and <sup>18</sup>O<sup>-</sup> were collected from the central part (20  $\mu$ m in diameter) of the sputtered area.



Fig. 1. SEM image of  $Ce_{0.9}Gd_{0.1}O_{1.95}$  (GDC) coated on the surface of  $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ .

#### 3. Results and discussion

#### 3.1. Enhancement of surface oxygen exchange kinetics $(k^*)$

The oxygen isotope ratio  $([^{18}O]/([^{18}O] + [^{16}O]))$  profile is shown in Figs. 2 and 3. The oxygen ratio from the samples was higher than the natural abundance of isotope oxygen (0.002) which indicates that the isotope exchange treatments were successful. At the low temperature (873 K) and low oxygen partial pressure  $(10^{-2} \text{ bar})$ , the exchange time was 30 min during isotope exchange treatment. The relatively long exchange time has been chosen since the isotope oxygen needs time to dissolve into the samples.



**Fig. 2.** Profile of oxygen ratio of (a) bare  $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$  and (b)  $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$  coated with  $Ce_{0.9}Gd_{0.1}O_{1.95}$  (GDC) at 1073 K under  $10^{-1}$  bar of  $p(O_2)$ . There is slightly enhancement of oxygen concentration on the  $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$  coated with  $Ce_{0.9}Gd_{0.1}O_{1.95}$  (GDC). The solid line indicates the curve fitting result.

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