DC-Voltage-Induced High Oxygen Permeation through a Lanthanum Silicate Electrolyte with a Cerium Oxide Thin Film

Shingo IDE,a,b,*,‡ Ken WATANABEC,t,‡ Koichi SUEMATSU,c,t,‡ Yasuhiro SETOB,‡†‡ Isamu YASHIMA,b,‡† and Kengo SHIMANOEa,c,‡

* Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
† Mitsui-Mining & Smelting Co., Ltd., 1333-2 Haraichi, Ageo, Saitama 362-0021, Japan
‡ Department of Advanced Materials Science and Engineering, Faculty of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan
* Corresponding author: s_ide@mitsui-kinzoku.com

ABSTRACT
An oxide-ion-conductor-based oxygen pumping system can serve as an on-site oxygen separation system. Herein, we present the oxygen permeation capability of a Pt electrode/La-Sm-doped CeO2 (L-SDC) intermediate layer/c-axis-oriented La0.66Sr0.33Ba0.7O3-δ (c-LSB0) solid electrolyte cell. A significant increase in the oxygen permeation flux is observed on applying a DC voltage of ≥4 V at temperatures <600 °C. A remarkably high flux of 5.2 mL cm⁻² min⁻¹ is obtained even at 500 °C. Furthermore, in situ x-ray diffraction studies under applied voltages reveal an increase in the lattice constant of L-SDC, accompanied by a drastic increase in the oxygen permeation flux, indicating the reduction of Ce⁴⁺ and formation of oxygen vacancies. These results suggest that the observed change in L-SDC under the applied voltage results in the in situ formation of a mixed electron- and oxide-ion-conducting L-SDC electrode, indicating that the oxygen reduction reaction and incorporation is significantly enhanced.

Keywords: Oxide Ion Conductor, Lanthanum Silicate Electrolyte, Cerium Oxide Thin Film, Oxygen Permeation

1. Introduction

Oxygen gas, which is often used in the industrial and medical fields, is produced by the cryogenic distillation method. It is mainly supplied as compressed oxygen gas or liquid oxygen in cylinders (e.g., 7000 L, 50–80 kg), and it requires periodic cylinder replacement and gas replenishment. Therefore, it is crucial to have an on-site oxygen gas supply system to prevent the shortage of oxygen supply during natural disasters or public health crises like COVID-19. Medical oxygen gas, which is used especially for patients with lung diseases, requires a high concentration supply because it requires an accurate concentration control. For on-site oxygen gas supply, methods like pressure swing adsorption (PSA) and membrane separation methods based on polymer and ceramic membranes are available. The oxygen separation method employing a ceramic membrane requires a high temperature and allows the supply of a higher oxygen concentration than that provided by the PSA method or a polymer membrane. There are two types of electrochemical oxygen separation methods employing the ceramic membranes at high temperatures, namely oxygen separation using mixed ionic-electronic conductors (MIECs) under an oxygen potential difference and oxygen pumping using oxide-ion conductors under DC bias. In particular, an oxygen gas pumping system is suitable as an on-site oxygen separator because the amount of high-concentration oxygen can be easily adjusted and the device can be miniaturized. Furthermore, oxygen pumping systems can not only be useful for on-site oxygen supply, but also for realizing carbon neutral technologies, such as water electrolysis and CO₂ electrolytic cells, as well as NH₃ synthesis applications. Therefore, we focused on oxygen pumping materials. Yttria-stabilized zirconia (YSZ) is widely used as an oxide-ion conductor. Several studies have demonstrated the oxygen pumping properties of YSZ when used as a solid electrolyte, and its oxide-ion conductivity (σO) at operating temperatures exceeding 700 °C. Solid electrolytes that exhibit high σO values in the low- and intermediate-temperature ranges (-600 °C) have been reported to reduce power consumption and heat-resistant component costs. Previously, the oxygen pumping properties of bismuth-oxide-based solid electro-
lys, which exhibit higher σo values than YSZ, have been reported.24-26 Cells with B2V0.0Cu0.0O3.5 solid electrolytes (0.074 Scm⁻¹ at 500 °C) exhibited an oxygen permeation flux of 2.6 mL cm⁻² min⁻¹ at 500 °C under a DC voltage of 4.0 V.24 Further, a Dy0.08W0.92Ba0.1O2 (0.13 Scm⁻¹ at 650 °C) solid electrolyte exhibited an oxygen permeation flux of 2.4 mL cm⁻² min⁻¹ at 600 °C under a DC voltage of 1.0 V.25 However, electron conductivity has been observed when a high voltage is applied due to the reduction of the solid electrolyte. Therefore, the oxygen permeation flux may decrease due to a decrease in the oxygen-ion transference number, which is a concern.26 An apatite-type lanthanum silicate (LSO) with a structure of the P6/m space group,27 which has a high σo was used as a solid electrolyte to obtain a higher oxygen permeation flux than that of the YSZ or bismuth-oxide-based solid electrolyte. LSO can be a promising solid electrolyte in the oxygen separation system because it not only has a high σo (0.01 Scm⁻¹ at 400 °C) along the c-axis,28 but also has a high oxide-ion transference number.29 We synthesized a La0.58Sr0.38Ba0.06O2.35 (c–LSBO) solid electrolyte with a crystal orientation along the c-axis and reported a high σo (0.016 Scm⁻¹ at 400 °C).30,31 Additionally, by employing c–LSBO in a novel oxygen separation device and gas sensor, our group demonstrated low- to-intermediate temperature operability.23,29 In terms of the oxygen pumping properties, cell resistance decreased by more than 80 % at a DC voltage of 2.0 V upon the inclusion of an intermediate Sm0.9Ce0.1O2 (SDC) thin film layer between the c–LSBO electrolyte and the Pt electrode, compared with that of the cell without the SDC. Furthermore, using a p-type oxide-based MIEC, La0.5Sr0.3Co0.7–

Nia0.0Fe0.0O2 electrolyte, a high oxygen permeation flux of 3.5 mL cm⁻² min⁻¹ was achieved at 600 °C and a DC voltage of 1.5 V.32 Further improvements in the oxygen pumping properties at low temperatures will significantly contribute to the realization of on-site oxygen supply and electrolysis technology. In this study, the oxygen permeation flux of a cell with the Pt electrode/L-SDC intermediate layer/c–LSBO solid electrolyte structure was investigated.

2. Experimental Method

2.1 Cell preparation

The c–LSBO solid electrolyte was prepared by reacting sintered La2SiO4 with Bi2O3 vapor at 1570 °C for 40 h in an electric vertical double furnace.30,31 The obtained c–LSBO was polished to a thickness of 350 µm. Then, the SDC intermediate layer (thickness: 200, 300, and 400 nm) was deposited on the cathode side surface of c–LSBO by radio frequency sputtering using a Ce0.9Sm0.1O2–δ sputtering target and annealed at 1400 °C for 1 h in air. Subsequently, 100 nm-thick Pt electrodes were deposited on both sides of the c–LSBO by the DC sputtering method, following which a layer of Pt paste was deposited by screen printing (area: 1.23 cm²) and calcined in air at 750 °C for 1 h. The cross-sections of the prepared samples were investigated by scanning transmission electron microscopy combined with energy-dispersive X-ray spectroscopy (STEM-EDS, JEM-ARM200F, JEOL Ltd., Tokyo, Japan) and field-emission scanning electron microscopy (FE-SEM, JSM-7900F, JEOL Ltd., Tokyo, Japan).

2.2 Oxygen permeation flux measurement

To measure the oxygen permeation flux, both sides of the prepared cell were sealed with Al2O3 tubes using an inorganic adhesive. Then, synthetic air (P0, 2.1 × 10⁴ Pa, PH2O: <22 Pa) and N2 (P0 = 5.1 Pa, PH2O: <2.4 Pa) were supplied to the cathode and anode (200 mL min⁻¹), respectively. An oxygen sensor (LC-450A, Toray, Japan) was used to measure oxygen concentration. To evaluate the leak oxygen, the oxygen concentration ([O2]leak) without applying the voltage was measured. Then, the oxygen concentration ([O2]perm) derived from the oxygen pumping under applying the voltage was estimated using Eq. (1):

\[ [O_2]_{\text{perm}} = [O_2]_{\text{LDC}} - [O_2]_{\text{leak}}. \] (1)

Here, [O2]LDC is the oxygen concentration under applying the voltage. I–V measurement was performed using a potentiostat (VSP, Bio-Logic Sciences Instruments, France) at 500 and 600 °C (Fig. 2a). The oxygen permeation flux (jO2, mL cm⁻² min⁻¹) was then determined using Eq. (2):

\[ j_{O_2} = \frac{Q_{NO_2} \cdot [O_2]_{\text{perm}} \cdot 10^{-6}}{S}, \] (2)

where QNO2 is the flow rate (scm) of N2 and S is the area of the electrode (cm²).

2.3 In situ XRD analysis under the applied voltages

The application of bias voltage resulted in changes in the crystal structure, which were studied by high-temperature X-ray diffraction (XRD, RINT-TTRIII, Rigaku Corporation, Tokyo, Japan) with a two-dimensional detector using CuKα radiation (λ = 1.5406 Å). A bias voltage of 0.5–4.7 V was applied using a potentiostat at 600 °C in air.

3. Results and Discussion

Figure 1 shows the cross-section of the interface between the intermediate thin film layer of L-SDC and c–LSBO electrolyte in a Pt/L-SDC/c–LSBO system. A dense, intermediate thin film was formed perpendicular to the c-axis of LSBO, i.e., the direction of oxygen-ion conduction of electrolyte. According to the EDS data, La in the electrolyte diffused to the SDC intermediate layer (Eq. (3)).

\[ La_{2}O_{3} + \frac{3}{2}e^{-2} \rightarrow 2La_{2}O_{5} + 3O^{2-} + V^{0} \] (3)

This was possibly caused by the interdiffusion of Sm and La during the high-temperature annealing at 1400 °C. The composition of the intermediate layer was determined to be La0.49Ce0.49Sm0.02O2–δ (L-SDC) by EDS analysis.

Figure 2 shows the I–V curves of the Pt/L-SDC/c–LSBO system. Consistent with the findings of a previous study,32 this system with an L-SDC intermediate layer exhibited higher current than the Pt/c–LSBO cell without the intermediate layer at 600 °C. As the DC voltage was increased, the current density increased by 4.8 times at 4.5–5.0 V, and the oxygen permeation flux was 5.2 mL cm⁻² min⁻¹. At 500 °C, the current density increased by more than 13 times at 8.0–8.5 V, and the corresponding oxygen permeation flux was 5.1 mL cm⁻² min⁻¹ (Fig. 2b). In contrast, no rapid increase in current was observed for the Pt/c–LSBO cell without the L-SDC layer, and the sample cracked when a voltage of 4.3 V was applied, thereby not allowing further measurements. The results imply that a drastic increase in current at a high voltage in the Pt/L-SDC/c–LSBO system is due to the effect of L-SDC used as the intermediate layer. The main conduction carriers are oxide-ion (Eq. (4)) as the oxygen permeation flux approaches the theoretical value calculated using the Faraday’s law (Fig. 2c).

\[ \frac{1}{2} O_{2} + 2e^{-} + V^{0} \rightarrow O^{2-} \] (4)

Moreover, the drastic increase in current was found to be reversible. In the second cycle, the current decreased than that in the first cycle in the entire applied voltage region; however, the I–V characteristics in the third cycle were equivalent to those in the second cycle (Fig. 2d).

To determine the effect of L-SDC, the influence of L-SDC layer thickness on the oxygen permeation and threshold voltage required to induce a drastic increase in oxygen permeation was investigated. Figure 3 presents the I–V characteristics of the systems with L-SDC layers of different thicknesses (200, 300, and 400 nm). As the film thickness decreased, the threshold voltage for inducing a drastic

Electrochemistry, (in press) 1–6
Figure 1. (a) Crystal structure of apatite-type La$_{0.33}$Si$_6$O$_{26}$. (b–c) STEM, (d) ADF-STEM, and (e–g) STEM-EDS mapping images of the interface between L-SDC and c-LSBO.

Figure 2. (a) Schematic of the evaluation method and cell structure of the Pt/L-SDC/c-LSBO system. (b) I-V data and (c) oxygen permeation flux at 500, 600, and 800 °C. (d) Three cycles of I-V measurements at 600 °C.
An increase in oxygen permeation decreased from 6.0 to 3.5 V, indicating that the threshold voltage depended strongly on the thickness of the L-SDC layer. The DC voltage range over which the current density increased varied drastically depending on the L-SDC film thickness. However, at a thickness of 200 nm, the current density after the threshold voltage was 44–50% lower than those of the other two cells with 300 and 400 nm-thick L-SDC layers. Moreover, even in the low-current-density region before the threshold voltage, the value was lower than those of the cells with thicker layers. Based on the analysis of surface morphology in the SEM images using a software, the surface coverage of c-LSBO with a 200 nm-thick L-SDC layer was found to be ~31%, while the surface coverage was determined to be almost 100% at the L-SDC layer thicknesses of 300 and 400 nm. This indicates that at a thickness of 200 nm, many sections of the L-SDC layer were electrically isolated and the utilization efficiency of the deposited L-SDC for oxygen permeation was lower than those of the thicker L-SDC layers. Hence, the fabrication of a thin L-SDC layer with high surface coverage on c-LSBO could decrease the threshold voltage at a high current density.

To understand the mechanism of drastic increase in the oxygen permeation flux under DC voltage, high-temperature XRD measurements were performed by applying a DC voltage at 600 °C (Fig. 4). The L-SDC (PDF Number 01-080-553) thin film layer showed the fluorite structure (Fm3m space group). The XRD peaks of the L-SDC layer shifted to lower 2θ values in the high DC voltage region, where the current density increased. In addition, an unknown peak appeared at DC voltages of 2.5–3.0 V and 4.5–4.7 V. Meanwhile, no significant changes were observed in the XRD pattern of c-LSBO (PDF number 01-074-9552). This result suggests that the structure...
of the intermediate L-SDC layer changed according to the current density when the DC voltage was applied at a high temperature. We attributed the decrease in current density between 3.5 and 4.0 V to an increase in mechanical contact resistance or L-SDC-layer-cracking during the measurement.

Figure 5 shows the relationship between the current density and lattice constant of L-SDC. When no DC voltage was applied (i.e., at 0 V), the lattice constant of L-SDC was 5.569 Å, which is comparable to that of La-substituted CeO₂ (Ce₀.₅₆La₀.₄₄)O₁.₇₈,18 and a compositional ratio similar to that of La-substituted CeO₂ (Ce₀.₅₆La₀.₄₄)O₁.₇₈ was obtained. This lattice constant of L-SDC suggests that La⁴⁺ diffused from LSBO and replaced Ce⁴⁺ in the SDC layer. Although the lattice constant of L-SDC did not change significantly in the low-current region, it increased slightly at the current density of ~0.10 A cm⁻² and then significantly with a further increase in current. This increase in lattice constant coincided with the appearance of an unknown peak in Fig. 4(c). Therefore, the appearance of the unknown peak is presumed to be due to the reduction in L-SDC. Moreover, a lattice constant of 5.567 Å was determined without any applied voltage after these measurements, which indicates that the change in the lattice constant was reversible and dependent on the applied current. The increase in the lattice constant suggests that Ce⁴⁺ (0.87 Å) was reduced to Ce³⁺ (1.01 Å) in the L-SDC layer when the DC voltage was applied, i.e., the electron conduction of L-SDC should increase due to the reduction of Ce⁴⁺ in the high-voltage region.35–37 Additionally, L-SDC should transform from an oxide-ion conductor to n-type MIEC, which conducts oxide-ions as well as electrons.38,39 Therefore, it can be inferred that the n-type MIEC formed in situ causes a drastic increase in the oxygen permeation flux at high applied voltages. We previously reported that the formation of an SDC interlayer with an isotropic oxide-ion conduction pathway enhanced the oxygen incorporation into c-LSBO from the triple phase boundary (TPB),32 as shown in Fig. 5. The rate-determining step of oxygen pumping through the c-LSBO-based cell appears to be the oxygen incorporation reaction.

4. Conclusions

The results obtained herein suggest that a drastic increase in the oxygen permeation flux induces the in situ formation of an n-type MIEC L-SDC layer at high DC voltages. In the case of an n-type MIEC electrode, the reaction site of oxygen incorporation into the solid is not only the TPB, but also the double-phase boundary (DPB) between the oxygen gas phase and the n-type MIEC. Thus, the formation of the n-type MIEC leads to enhanced oxygen permeation flux. Additionally, the MIEC electrode enhances the oxygen permeation capability of the c-LSBO-based cell more than the Pt electrode does. Therefore, we speculate that the in situ-formed MIEC electrode significantly increased the oxygen permeation flux with the application of a DC voltage. Furthermore, the wide electrochemical window of c-LSBO allows the high oxygen permeation phenomenon under the applied DC voltage. In the future, we expect to achieve a higher oxygen permeation flux at a lower temperature and applied voltage by optimizing the composition, morphology, and thickness of the intermediate layer.

Author Contributions

The manuscript was written through contributions of all the authors. All the authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interests.

References

1. R. L. Cornelissen and G. G. Hirn, *Energy Convers. Manage.*, 39, 1821 (1998).
2. S. Kobayashi, M. Hanagama, S. Yamada, and M. Yanai, *Eur. Respir. J.*, 39, 1047 (2012).
3. World Health Organization (WHO), Oxygen Sources and Distribution for COVID-19 Treatment Centres, *WHO Guide*, 2020, April 1–6, https://www.who.int/publications/i/item/oxygen-sources-and-distribution-for-covid-19-treatment-centres
4. J. D. Sherman, *Proc. Natl. Acad. Sci. U.S.A.*, 96, 3471 (1999).
5. T. H. Kim, W. J. Koros, G. R. Husk, and K. C. O'Brien, *J. Membr. Sci.*, 37, 45 (1988).
6. L. M. Robeson, *J. Membr. Sci.*, 62, 165 (1991).
7. Y. Teraoka, H.-M. Zhang, S. Furukawa, and N. Yamazoe, *Chem. Lett.*, 14, 1743 (1985).
8. K. Watenabe, M. Yuasa, T. Kida, Y. Teraoka, N. Yamazoe, and K. Shimamoe, *Adv. Mater.*, 22, 2267 (2010).
9. D. Yuan and F. A. Krüger, *J. Electrochem. Soc.*, 116, 594 (1969).
10. A. V. Spirin, A. V. Nikonov, A. S. Lipilin, S. N. Paranin, V. V. Ivanov, V. R. Khurstov, A. V. Valentsev, and V. I. Knutikov, *Russ. J. Electrochem.*, 47, 569 (2011).
11. Q. Pham and R. S. Glass, *Electrochim. Acta*, **43**, 2699 (1998).
12. K. R. Sridhar and B. T. Vaniman, *Solid State Ionics*, **93**, 321 (1997).
13. T. A. Volsko, *Respir. Care*, **64**, 723 (2019).
14. N. Q. Minh, *J. Am. Ceram. Soc.*, **76**, 563 (1993).
15. A. O. Isenberg, *Solid State Ionics*, **3–4**, 431 (1981).
16. F. Bidrawn, G. Kim, G. Corre, J. T. S. Irvine, J. M. Vohs, and R. J. Gorte, *Electrochem. Solid-State Lett.*, **11**, B167 (2008).
17. A. Fernandez, N. M. Hortance, Y. H. Liu, J. Lim, K. B. Hatzell, and M. C. Hatzell, *J. Mater. Chem. A*, **8**, 15591 (2020).
18. R. M. Ormerod, *Chem. Soc. Rev.*, **32**, 17 (2003).
19. J. A. Kilner, *Solid State Ionics*, **129**, 13 (2000).
20. J. C. Boivin and G. Mairesse, *Chem. Mater.*, **18**, 2870 (1998).
21. J. C. Boivin, C. Piruvano, G. Nowogrocki, G. Mairesse, P. Labrune, and G. Lagrange, *Solid State Ionics*, **113–115**, 639 (1998).
22. H. Okudera, Y. Masubuchi, S. Kikkawa, and A. Yoshiasa, *Solid State Ionics*, **176**, 1472 (2005).
23. T. Ishihara, H. Matsuda, and Y. Takita, *J. Am. Chem. Soc.*, **116**, 3801 (1994).
24. M. H. Paydar, A. M. Hadian, and G. Faifi, *J. Mater. Sci.*, **41**, 1953 (2006).
25. J. C. Boivin, C. Pirovano, G. Nowogrocki, G. Mairesse, P. Labrune, and G. Lagrange, *Solid State Ionics*, **113–115**, 639 (1998).
26. J. B. Goodenough, A. Manthiram, M. Paranthaman, and Y. S. Zhen, *Mater. Sci. Eng., B*, **12**, 357 (1992).
27. E. Zintl and U. Croatto, *Z. Anorg. Allg. Chem.*, **242**, 79 (1939).
28. E. B. Lavik, I. Kosacki, H. L. Tuller, Y. M. Chiang, and J. Ying, *J. Electroceram.*, **1**, 7 (1997).
29. H. L. Tuller and A. S. Nowick, *J. Electrochem. Soc.*, **122**, 255 (1975).
30. R. Doshi, Y. Shen, and C. B. Alcock, *Solid State Ionics*, **68**, 133 (1994).
31. Z. A. Feng, F. El Gabaly, X. Ye, Z. X. Shen, and W. C. Chueh, *Nat. Commun.*, **5**, 4374 (2014).
32. Y. Cho, M. Ogawa, I. Oikawa, H. L. Tuller, and H. Takamura, *Chem. Mater.*, **31**, 2713 (2019).