Oxygen pumping based on oxide ionic conductors

Fast ion conductors
Control of interface
Design of Electrode Materials

Journal of the Ceramic Society of Japan
2019
Oxygen pumping based on c-axis-oriented lanthanum silicate ceramics: challenge toward low operating temperature

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A new electrochemical oxygen separation pump was developed by using c-axis-oriented La0.68Si6.3B0.7O26.14 (c-LSBO), which has high oxide-ionic conductivity (>10⁻³ S cm⁻¹) up to 300°C. Interfacial resistance between the electrode and c-LSBO was investigated to realize the full potential of LSBO as an oxygen separation material. The formation of a Sm-doped CeO₂ (SDC) thin film (thickness: 300 nm) between the electrode and c-LSBO was effective for suppressing the interfacial resistance. Furthermore, a mixed conductive La0.7Sr0.3Co0.7Fe0.3O1.9 (SDC) was applied to the electrode for enhancing the oxygen reduction/evolution activity on the electrode. The LSCF/SDC/c-LSBO symmetric cell showed an oxygen permeation flux of 3.5 mL cm⁻² min⁻¹ (1.0 A cm⁻²) at 600°C under an applied DC voltage of 1.5 V; this value was 67 times that of Pt/c-LSBO. This oxygen pump based on the LSCF/SDC/c-LSBO symmetric cell could find promising application in oxygen separation at intermediate temperatures. Further reduction of the interfacial resistance and polarization resistance of the electrode may decrease the operating temperatures to below 400°C.

Key-words : Oxygen separation, Oxide-ionic conductor, Mixed conductor, C-axis-oriented lanthanum silicate

Demands for a portable oxygen separation system are increasing for applications in home healthcare systems for lung disease and gas-cylinder-free oxygen masks for emergency use. Oxygen pumping based on oxide-ionic conductors allows for the spontaneous separation of oxygen from air under an applied DC bias, so this concept can be adopted to design compact, low-cost oxygen separation systems.1) In addition, the oxygen pumping system is widely used in solid oxide fuel cells,2) water electrolysis,2) and amperometric gas sensors3) and is hence a key electrochemical device in the energy, environmental, and medicine industries. In general, yttrium stabilized zirconia (YSZ) has been widely used as a solid electrolyte for a long time, and an oxygen pumping device based on YSZ has been reported.4) However, the high operating temperature (800°C) of the system, which is due to the low oxide-ionic conductivity of YSZ at lower temperatures, necessitates high power. Hence, for reducing power consumption, it is desirable to develop a new oxide ion conductor with higher ionic conductivity.

Till date, many kinds of oxide ionic conductors for low operating temperatures have been reported5)–10) and oxygen separation at intermediate temperatures around 600°C has been also demonstrated.11)–13) Among them, Hong et al. recently reported an excellent oxygen pumping system based on the Dy0.08W0.04Bi0.88O2–δ (DWBO) electrolyte, which shows a high oxide ionic conductivity of 0.13 S cm⁻¹ at 650°C, with a La0.6Sr0.4MnO3–δ/DWBO composite electrode, and demonstrated a high oxygen flux of 2.4 mL cm⁻² min⁻¹ under a DC of 1.0 V at 600°C.13) This result strongly indicates that the high oxide ionic conductivity of the electrolyte plays an important role in design of a low-power consumption oxygen separation system. Hence, the use of a material whose oxide ionic conductivity exceeds that of DWBO can lead to a further reduction in the operation temperature.

With this background, we focused on La9.33Si6O26 (LSO), which has a hexagonal apatite-type structure with a fast oxygen diffusion path along the c-axis. The oxide ionic conductivity along the c-axis has been reported to be 1–2 orders of magnitude higher than that across the c-axis.14) Fujii et al. reported that La0.31Si3.82O26 single crystal displays remarkably high oxide ionic conductivity of 1.04 x 10⁻² S cm⁻¹ at 400°C.15) In addition, the fabrication process for c-axis-oriented LSO ceramics with high...
ionic conductivity has been developed.\(^{14,16,17}\) Therefore, c-axis-oriented LSO seems to be a promising candidate for the solid electrolyte of oxygen separation systems operating at 400°C. However, the oxygen separation performance achieved using c-axis-oriented LSO has not been probed because of the lack of electrode materials that are applicable for LSO with low interfacial resistance and polarization resistance. Herein, we designed an electrode for oxygen pumping based on c-axis-oriented LSO ceramics and attempted to reduce the interfacial resistance between the Pt electrode and the electrolyte by depositing an interlayer based on a Sm-doped CeO\(_2\) thin film, which is also a high ionic conductor. For further reducing the polarization resistance of the electrode, a mixed oxide and electrically conductive material La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.78}\)Ni\(_{0.02}\)Fe\(_{0.2}\)O\(_{3-\delta}\) (LSCFN), which has been reported as an electrode material with a high oxygen reduction/evolution activity for the potentiometric solid electrolyte gas sensor,\(^{13,19}\) was employed as the electrode material.

The c-axis-oriented La\(_{0.6}\)Sr\(_{0.4}\)Co\(_{0.78}\)Ni\(_{0.02}\)Fe\(_{0.2}\)O\(_{3-\delta}\) ceramic (c-LSBO) was fabricated by using boron vapour and a lanthanum silicate disk at 1570°C.\(^{15}\) The theoretical density of the obtained disk was more than 97% and the oxide ionic conductivity at 600°C was \(6.3 \times 10^{-2}\) Sc m\(^{-1}\). The details of fabrication of c-LSBO will be reported in near future. To fabricate a symmetric cell for the evaluation of the electrochemical performance, the thickness of the pellet was set to 350 μm by polishing with diamond slurry. A Sm-doped CeO\(_2\) (SDC) interlayer was deposited on the both surface of c-LSBO by sputtering, followed by and then annealed at 1400°C. Pt was deposited on the surface of c-LSBO with or without SDC by a screen-printing method. The obtained sample was dried and calcined at 120 and 750°C, respectively. For comparison, a Pt/YSZ symmetric cell was fabricated. LSCFN powder was prepared by the amorphous malic acid precursor method.\(^{20}\) La(NO\(_3\))\(_2\), Sr(NO\(_3\))\(_2\), Co(NO\(_3\))\(_2\), Ni(NO\(_3\))\(_2\), and Fe(NO\(_3\))\(_3\) in stoichiometric ratio were dissolved in deionized water, and then a solution containing malic acid as a complexing agent was added. The molar ratio of malic acid to the total metal ions was set to 1.5. The pH of the mixed solution was adjusted to 6 using NH\(_3\) solution. The mixed solution was evaporated and dried at 300–350°C on a hot plate, and the obtained powder was calcined at 900°C for 5 h. X-ray diffraction (XRD, RINT2100: Rigaku, Japan) analysis confirmed that LSCFN had a trigonal perovskite-type structure without any impurity. The LSCFN electrode was also deposited on c-LSBO with SDC by screen-printing and calcined at 900°C for 5 h. Pt was deposited on the LSCFN electrode as current collector by screen-printing, followed by calcination at 750°C for 5 h. The thickness of the Pt layer and LSCFN electrode was about 10 μm.

The electrochemical performance of the fabricated symmetric cell at 600°C was evaluated by AC impedance spectroscopy (Solartron 1260/1287; Solartron, USA) from 0.5 to 300 kHz and DC polarization measurements from 0.1 to 2 V (HZ-3000; Hokuto Denko Co., Japan). The oxygen permeation flux was evaluated by a home-built setup. The symmetric cell was fixed to an Al\(_2\)O\(_3\) tube by an inorganic adhesive. For permeation tests, synthetic air (200 mL min\(^{-1}\)) and N\(_2\) (200 mL min\(^{-1}\)) were flowed to each side of the symmetric cell, and DC voltage was supplied by a potentiostat (Solartron 1287; Solartron, USA). Oxygen passing through the symmetric cell from the air side to the N\(_2\) side was monitored by an oxygen sensor (LC-450A; Toray, Japan).

**Figure 1(a)** shows the impedance spectra for the Pt/c-LSBO and Pt/SDC/LSBO symmetric cells at 600°C, from which the total resistance for these cells is estimated to be 99 and 18 Ω cm\(^2\), respectively. It is obvious that both interfacial resistance and polarization resistance are drastically reduced by the formation of the SDC interlayer. Figure 1(b) shows the DC polarization curves for Pt/c-LSBO and Pt/SDC/c-LSBO at 600°C, along with the result for the Pt/YSZ symmetric cell for comparison [Fig. 1(b)]. The current density of Pt/c-LSBO, Pt/SDC/c-LSBO, and Pt/YSZ under 1.5 V is 23, 143, and 38 mA cm\(^{-2}\), respectively. The obtained ionic current of Pt/c-LSBO is smaller than that of Pt/YSZ, although the oxide ionic conductivity of c-LSBO is one order of magnitude higher than that of YSZ. Because we use the same Pt electrode for all the electrolytes, the oxygen reduction/evolution activity of the electrode through Pt/c-LSBO and Pt/YSZ is considered to be the same. Thus, this result indicates that interfacial resistance of Pt/c-LSBO is one order of magnitude as higher than that of Pt/YSZ. In the case of c-LSBO, the fast ion path is limited along the c-axis.\(^{13}\) Thus, the ionized oxide ion should migrate from the triple phase boundary to the fast oxide ion path through...
the slow oxide ion diffusion path, as shown in Fig. 2(a). In contrast, the oxide ion can migrate isotopically through YSZ because of its cubic structure. Thus, it is likely that the interfacial resistance of c-LSBO becomes higher than that of YSZ. On the other hand, Pt/SDC/c-LSBO exhibits the highest current density under all the bias conditions among the three samples. The SDC shows an isotopic oxide ion path and its oxide ion conductivity (≈10⁻² S cm⁻¹) is much higher than that across the c-axis of c-LSBO (≈10⁻⁴ S cm⁻¹). Thus, we believe that the ionized oxide can be directly transported to the fast diffusion path in c-LSBO from the triple-phase boundary through SDC, as shown in Fig. 2(b), thus reducing the interfacial resistance remarkably. However, the mechanism underlying this reduction needs to be investigated in a future study.

To improve the electrochemical performance of the c-LSBO symmetric cell, a mixed conductive LSCFN, which has higher oxygen reduction/evolution reactivity, was applied as the electrode material. Figure 3(a) shows the impedance spectra for the LSCFN/SDC/c-LSBO and Pt/SDC/c-LSBO symmetric cells at 600°C. The total resistance of LSCFN/SDC/c-LSBO was 4.6 Ω cm² and the polarization resistance was much lower than that of Pt/SDC/c-LSBO, due to its high oxygen reduction/evolution activity. Figure 3(b) shows the results of DC polarization measurements for the LSCFN/SDC/c-LSBO and Pt/SDC/c-LSBO symmetric cells at 600°C. In the applied voltage range, the current density drastically increased when using LSCFN as the electrode. The current density of LSCFN/SDC/c-LSBO at 1.5 V was 1 A cm⁻² (oxygen flux: 3.5 mL min⁻¹ cm⁻²), which was 10 times higher than that of Pt/SDC/c-LSBO. This value is almost comparable to the oxygen flux of YSZ operating at 800°C. In addition, oxygen permeation tests revealed that the obtained oxygen flux is in good agreement with the theoretical value according to Faraday’s law, indicating that LSCFN/SDC/c-LSBO symmetric cell can separate oxygen from air without any side reaction in the applied voltage range (0.1 to 2 V).

Finally, DC polarization measurements were performed for 10 h to evaluate the stability of the symmetric cell. Figure 4 shows the time dependence of the current density under applied DC voltage of 1 and 1.5 V for LSCFN/SDC/c-LSBO symmetric cell at 600°C in air.
increase in the current density was observed at the initial stage. Thus, from the viewpoint of stability, the LSCFN/SDC/c-LSBO symmetric cell shows excellent performance as an oxygen pumping device. To the best of our knowledge, this is the first report of an oxygen pump based on c-LSBO, although our results are still limited to 600°C. According to our findings, however, we strongly believe that improvement on surface modification of c-LSBO with the materials that show a relatively high oxide ionic conductivity and development of novel mixed conductive electrode materials that show a high oxygen reduction/evolution activity even at low temperatures make it possible to operate the innovative oxygen pump at low temperatures.

In conclusion, we have developed for the first time a c-LSBO-based oxygen pump operating at 600°C. Two important factors played a role in achieving a high oxygen flux: 1) decreased interfacial resistance between the electrode and c-LSBO by the formation of an SDC interlayer; 2) the lower polarization resistance of the mixed conductive LSCFN electrode as compared to that of a Pt electrode. The LSCFN/SDC/c-LSBO symmetric cell exhibited a high oxygen flux of 3.5 mL min⁻¹ cm⁻² (1 A cm⁻²) under 1.5 V at 600°C with highly stability. Thus, it can be concluded that c-LSBO is a promising electrolyte for low-temperature-operating oxygen pump, gas sensor, and solid oxide fuel cell.

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