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Oxygen-ion Transfer between YSZ/YSZ and YSZ/LSCF under Mechanical Contact Stress

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The present study concerns oxygen-ion transfer between yttria-stabilized zirconia single crystals (YSZ/YSZ) under mechanical contact stress. Two YSZ single crystal plates were piled up between platinum meshes, and contact stress was mechanically applied. The interfacial conductivity as well as the bulk conductivity was successfully measured with this setup. The interfacial conductivity is greatly influenced by the contact stress, whereas the bulk conductivity is almost independent of the stress. The interfacial conductivity was significantly increased with increasing contact stress. A similar improvement in the interfacial conductivity between YSZ and lanthanum strontium cobalt ferrite (YSZ/LSCF) was also observed.

Introduction

Yttria stabilized zirconia (YSZ) is known as an oxygen-ion conducting material and one of the common electrolyte materials for solid oxide fuel cell (SOFC) due to its good ionic conductivity as well as chemical and mechanical stabilities.

For polycrystalline YSZ, the oxygen-ion transport property is attributed to the oxygen ion conductivities of bulk (grain) and grain boundary, and it has been generally known that oxygen-ion conductivity in bulk is superior to that in grain boundary (1,2). The oxygen-ion transport characteristics of the grain boundary in YSZ are normally extracted from the characteristics of polycrystalline samples, whereas it has been also evaluated using bicrystal or two single crystals in previous studies (3-5). Dragoo et al. evaluated the characteristics of the grain boundary by using YSZ bicrystal consisting of two single crystals and a single grain boundary and observed a large resistance of the grain boundary (3). Nakagawa et al. confirmed a blocking effect of the grain boundary by measuring the oxygen-diffusion behavior of YSZ bicrystal (4). Fabry et al. employed two YSZ single crystals mechanically contacting each other. A direct oxygen ion transfer between YSZ/YSZ involving no neutral oxygen atom was confirmed (5), although a large resistance due to the interface between YSZ/YSZ was obtained. The effect of the contact stress between two YSZ single crystals, however, was not considered in those studies.

Not only grain boundary, but also oxygen-ion transfer at every interface, for instance between electrolyte/electrode in SOFC, is an important issue. In most cases, an interface is subjected to contact stress (pressure); however its effect on the oxygen-ion transfer has not been quantitatively considered. For assessment of the oxygen-ion transfer at an interface under various contact stresses, a testing method should be established.

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In the present study, the oxygen-transfer between YSZ single crystals was investigated under mechanical contact stress. First, the evaluation method is proposed. Then, the interfacial conductivity between YSZ and YSZ single crystals was investigated. In addition, the interfacial conductivity between YSZ and lanthanum strontium cobalt ferrite (LSCF), which is one of common electrode materials for SOFC, is investigated with using the proposed method.

Experimental Procedure

13 mol%-yttria-stabilised zirconia single crystal plate (Dalian Optoelectronic Technology) was used in the present experiment. The dimension of the original plate was 25×25×1.0 mm^3 and the surfaces had (110) crystal orientation with a surface roughness of less than 1 nm. Various sizes of specimens were cut out from the plate using a diamond wheel saw.

For measuring impedance under contact stress, two different specimen configurations were employed, as illustrated in Fig. 1. In Config A shown in Fig. 1(a), which is similar to the configuration used in the literature (5), two small square plates (YSZ1 and YSZ2) with a size of 5.0×5.0×1.0 mm^3 were piled up between platinum (Pt) meshes with attached Pt wires which were connected to a chemical impedance meter (3532-80, Hioki E.E.). The whole Config A was placed inside a furnace of a material testing machine (1362, Instron). The temperature ranged from ~590 K to ~790 K, while the compressive load of 20 to 420 N (equivalent to 18 MPa of contact stress for Config A) was applied at each temperature. For the impedance measurement, the two-terminal method was employed (terminals I and II in Fig. 1(a)) and the frequency ranged from 10 Hz to 1 MHz. The measurement was conducted during unloading.

Config B shown in Fig. 1(b) consisted of a small plate (YSZ3, 5.0×2.5×1.0 mm^3) and a large plate (YSZ4, 15×10×1.0 mm^3). YSZ4 with platinum paste on the bottom was placed on a dummy small plate (YSZ5) and a temporary plate (dashed line). The whole Config B was placed inside the furnace, the preload of 5 N was applied, and the temporary plate was removed. The compressive load was varied from 5 N to 405 N (equivalent to 37 MPa of contact stress for Config B) at each temperature. The impedance was measured using the terminals I and II for evaluation of interfacial characteristics, and also terminals I and III as a temperature reference.

It should be noted that, in the measurement with Config A, a sum of the bulk impedances of YSZ1 and YSZ2 including the interfacial impedance between YSZ1 and YSZ2 were measured, whilst the bulk impedance of YSZ3, the partial impedance of YSZ4, and the interfacial impedance between YSZ3 and YSZ4 in Config B. All tests were carried out in air. Further experimental detail is given in (6).

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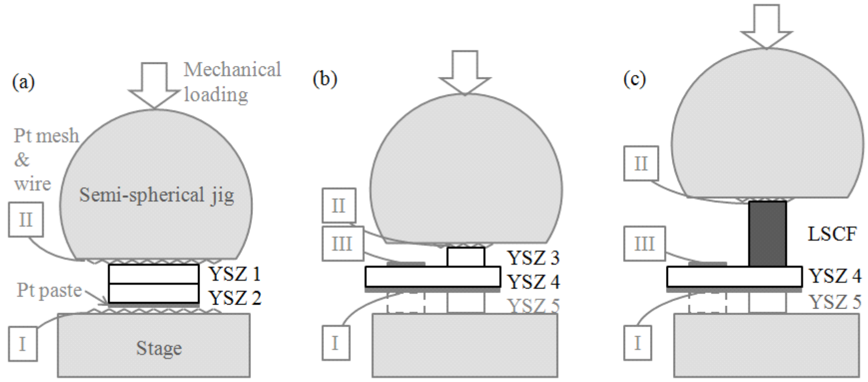

Figure 1. Experimental setup: (a) Config A (YSZ/YSZ), (b) Config B (YSZ/YSZ), (c) Config B (YSZ/LSCF).

With using Config B, the interfacial characteristics between YSZ and $La_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was also investigated as illustrated in Fig.1(c). LSCF sample was prepared in IEK-2, Jülich Forschungszentrum (7), and has a rectangular shape with the size of about 3.0×3.0×6.0 mm^3.

Results and Discussion

Config A (YSZ/YSZ)

Figure 2 shows the Nyquist plots obtained during unloading from 18 MPa to 3 MPa at 597 K using Config A. Two semi-circles are clearly observed for all cases, and the lower-frequency arc is always larger than the higher-frequency arc. During unloading, the lower-frequency arc becomes larger, whereas the higher-frequency arc remains almost unchanged. Below the stress of ~5 MPa, the higher-frequency arc almost cannot be separately observed because of the large lower-frequency arc as has been reported in earlier studies (3,5); however, in those studies, mainly/only a huge lower-frequency arc was observed due to a lack of a sufficient contact stress. The higher-frequency arc can be assigned to the bulk response (YSZ1 and YSZ2), whereas the lower-frequency arc to the interfacial resistance between the two single crystals. Further detail is given in (7). Although the bulk and interfacial resistances were successfully measured using Config A, contact stress higher than 18 MPa caused fracture of YSZ samples. Thus, Config B was developed in order to apply higher stress.

Config B (YSZ/YSZ)

Figure 3 shows the Nyquist plots of YSZ/YSZ measured during unloading at various temperatures using Config B. The contact stress up to 37 MPa was successfully applied without fracturing samples. The semi-circles were observed for 597 K and the higher-frequency arc related to R_{blk} seems to be constant. Also, the overall contact seems to be better in Config B than that in Config A. The lower-frequency arc related to R_{intf} with 37 MPa of contact stress at 597 K is very small, and the higher-frequency arc disappears at higher temperatures, particularly with higher stress. Figure 4 summarizes the variations of R_{intf} at 597 K with the contact stress obtained using Config B, where R_{intf} was calculated assuming that R_{blk} is independent of the contact stress. R_{intf} drastically

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decreases with contact stress below 5 MPa (insert in Fig. 4(a)) and it gradually decreases with stress above 5 MPa, which is estimated to be saturated at higher stress.

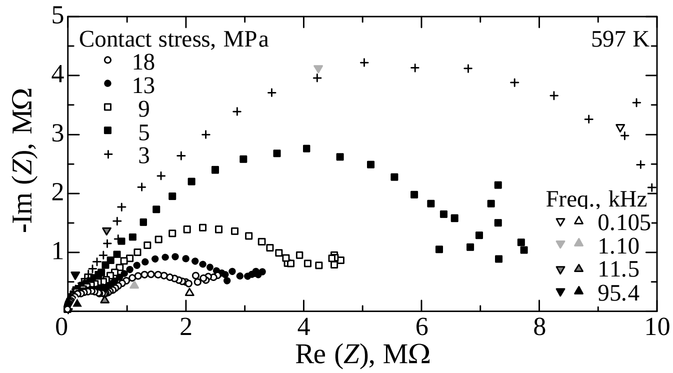

Figure 2. Nyquist plots at 597 K obtained with Config A.

Config B (YSZ/LSCF)

Figure 5 shows the Nyquist plots of YSZ/LSCF system measured during unloading at various temperatures using Config B. Similarly to the above case (YSZ/YSZ), two semi-circles were observed at 597 K, which again indicates that R_{blk} and R_{intf} (YSZ/LSCF here) were successfully measured. Figure 6 summarizes the variations of R_{intf} at 589 K with the contact stress obtained using Config B, where R_{intf} was calculated assuming that R_{blk} is independent of the contact stress. R_{intf} drastically decreases with contact stress below 5 MPa (insert in Fig. 6(a)) and it gradually decreases with stress above 5 MPa.

Discussion

Figure 7 shows the Arrhenius plots of the interfacial conductivities of YSZ/YSZ and YSZ/LSCF, which were calculated by using saturated resistance values at higher stress estimated from Figs. 4 and 6 and also the contact areas. The conductivity of YSZ/LSCF is slightly higher than that of YSZ/YSZ, although this difference could be within the experimental error. The activation energies for both cases are similarly 105~107 kJ/mol, which is also comparable to the reported value for mechanically-contacted YSZ/YSZ system and grain boundary (13). This result seems to imply that the interfacial characteristic of YSZ could be a limiting factor. Detailed discussion regarding the interface characteristics of YSZ/YSZ allowing for capacitance can be found in (7).

The reason for the change of the interface characteristics with the contact stress is briefly discussed. The most reasonable explanation for the enhancement of the conductivity with contact stress could be that an enlargement of the actual contact area between YSZ/YSZ or YSZ/LSCF has increased the apparent conductivity; however, as illustrated in Figs. 2, 3 and 5, the contact stress increases only the interfacial conductivity almost without changing the bulk conductivity. This implies that an appropriate contact for the measurement of the bulk conductivity is already achieved with stress as small as ~ 5 MPa. The present experimental result therefore indicates that the observed increase of interfacial conductivity could be not an apparent increase due to the enlargement of the contact area but possibly an intrinsic enhancement due to the contact stress between the YSZ plates. The origin of the intrinsic enhancement is still under investigation.

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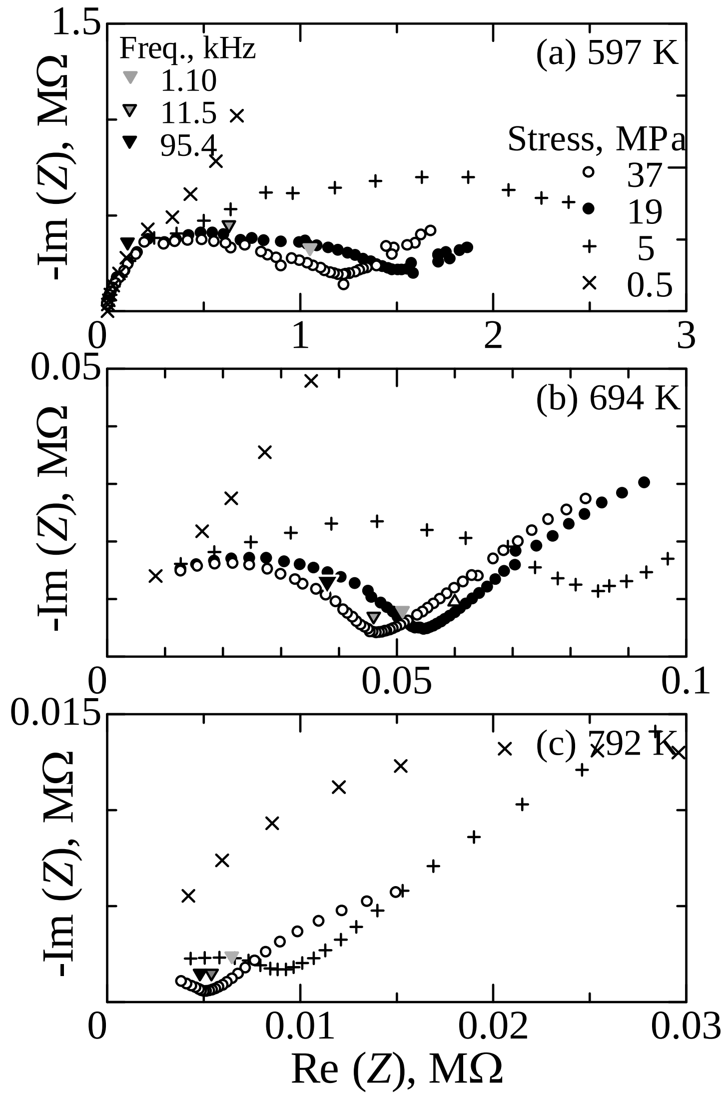

Figure 3. Nyquist plots obtained with Config B.

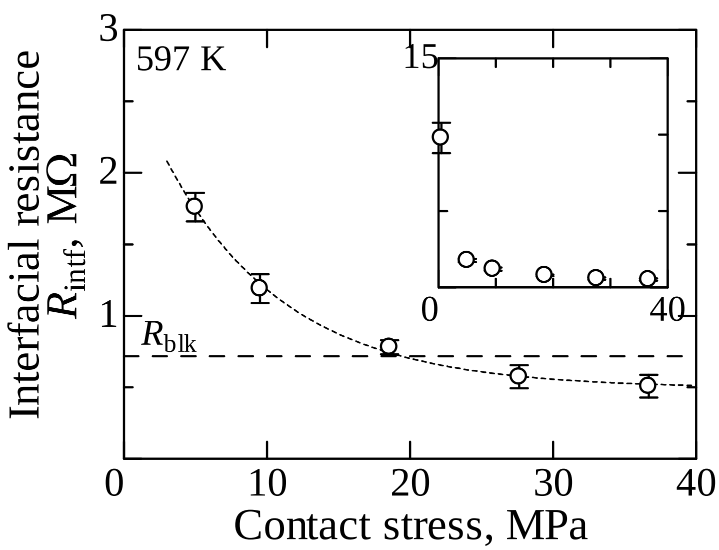

Figure 4. Interfacial resistance at 597 K obtained with Config B.

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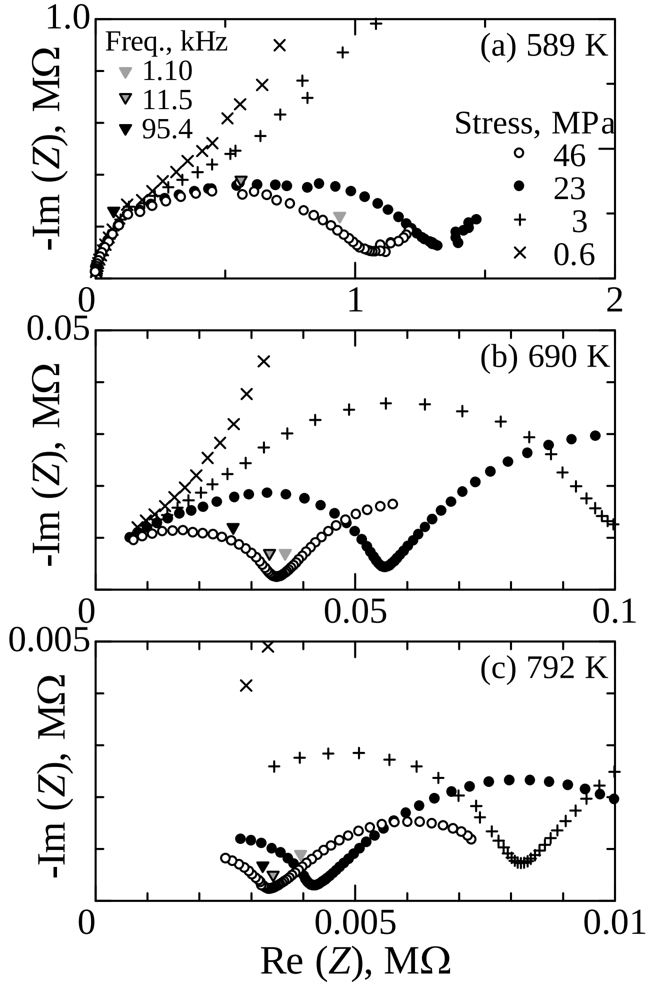

Figure 5. Nyquist plots obtained with Config B (YSZ/LSCF).

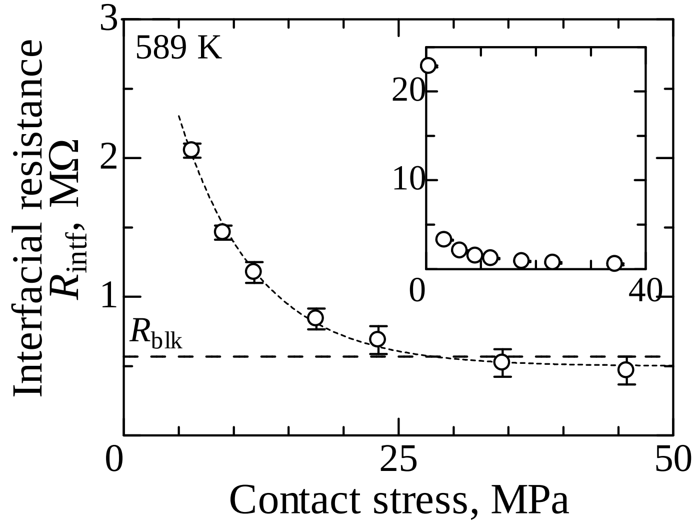

Figure 6. Interfacial resistance at 597 K obtained with Config. B (YSZ/LSCF).

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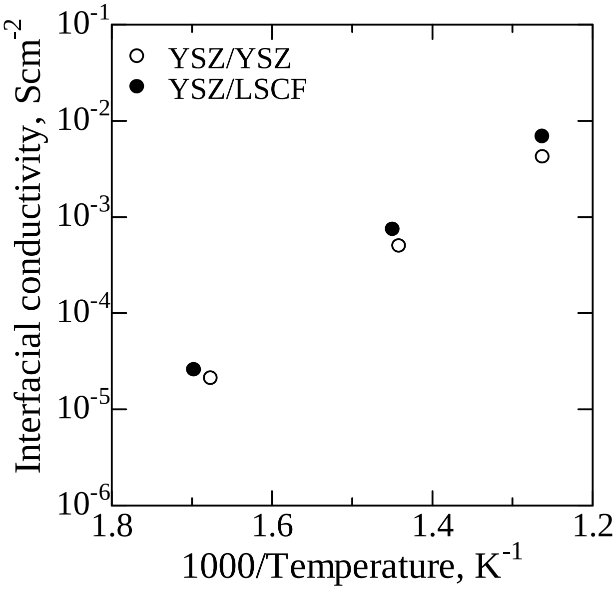

Figure 7. Arrhenius plots of interfacial conductivities.

Conclusion

The present study concerns oxygen-ion transfer between yttria-stabilized zirconia single crystals (YSZ/YSZ) under mechanical contact stress. The interfacial conductivity as well as the bulk conductivity was separately measured with the proposed setup. The interfacial conductivity was greatly influenced by the contact stress, whereas the bulk conductivity was almost independent of the stress. The interfacial conductivity was significantly increased with increasing contact stress, and it was gradually saturated with the stress around 40 MPa. The interfacial conductivity between YSZ and lanthanum strontium cobalt ferrite (YSZ/LSCF) was also investigated using the same set up. A similar improvement in the interfacial conductivity was observed under the contact stress.

Acknowledgments

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References

1. S.P.S. Badwal, *J. Mater. Sci.* **19**, 1767 (1984).
2. S.P.S. Badwal and J. Drennan, J. Mater. Sci. **22**, 3231 (1987).
3. A.L. Dragoo, C.K. Chiang, A.D. Franklin, J. Bethin, *Solid State Ionics* **7**, 249 (1982).
4. T. Nakagawa, I. Sakaguchi, N. Shibata, K. Matsunaga, T. Yamamoto, H. Haneda, Y. Ikuhara, *J. Mater. Sci.* **40**, 3185 (2005).
5. P. Fabry, E. Schouler, M. Kleitz, *Electrochim. Acta* **23**, 539 (1978).
6. W. Araki, *Electrochim. Acta* (accepted in Jul 2013).
7. W. Araki, J. Malzbender, *J. Euro. Ceram. Soc.* **33**, 805 (2013).

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