Relationship between thermal environment and conductivity enhancement under millimeter-wave irradiation heating of zirconia ceramics

Akira KISHIMOTO, Koyo SHIMOYAMA, Takashi TERANISHI and Hidetaka HAYASHI

Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan

Improving the conductivity of 8 mol % yttria-stabilized zirconia (8YSZ) electrolyte has enabled a lowering of the operating temperature of solid oxide fuel cells. We previously reported that millimeter-wave irradiation heating increases the ionic conductivity of ceramics. The ionic conductivity of 8YSZ under millimeter-wave irradiation heating had been up to 20 times higher than that with conventional heating. In the present study, we investigated the optimal thermal environment for millimeter-wave irradiation heating. We also investigated the thermal profile of samples under millimeter-wave irradiation heating to elucidate the rate of the non-thermal effect.

Key-words : Zirconia, Ionic conduction, Millimeter-wave, Thermal environment

1. Introduction

Solid oxide fuel cells (SOFCs) are of particular interest for their high efficiencies and simple configurations. Power generation efficiency increases with operating temperature because of decreasing ohmic loss with increasing electrolyte conductivity. Operation at high temperatures, such as 1000°C, requires expensive thermal resistance materials. Such severe operation conditions accelerate corrosion and lead to long-term instability. Maintaining a high efficiency at a low operating temperature requires improved electrolyte conductivity. Fast oxide ion or proton conductors have been explored for this reason, and various types of additives have been explored to modify the properties of ionic conductors.

As an alternative approach to improve the conductivity through novel materials, we have focused on improving the heating method. Microwave heating, including the millimeter-wave (MMW) variety, generates heat as the material interacts with the electromagnetic waves. Conventional SOFCs are heated with conventional electric heaters. MMW heating is commonly used in ceramics applications, in particular for sintering, because it can provide rapid and selective heating.

The application of MMW irradiation to SOFCs could provide rapid, on-demand heating, which is difficult with conventional approaches. Because MMW could selectively heat the SOFC electrolyte while maintaining the other components at a low temperature, the number of material candidates widens and could potentially lower the cost of fabrication. Additionally, MMW irradiation facilitates atomic transportation through a non-thermal effect.

We previously reported conductivity enhancements of various materials under millimeter-wave irradiation heating that is probably related to the non-thermal effect. In the present study, the temperature profiles of MMW irradiation-heated samples were examined by changing the thermal environment. The conductivity enhancement under MMW irradiation was compared with the thermal profile to identify the thermal and non-thermal effects. The optimal thermal environment providing the maximum ionic conductivity was identified.

2. Experimental procedure

Commercial 8 mol % yttria-stabilized zirconia powder (8YSZ; TZ-8Y; Tosoh, Japan) was used as the starting powder. A predetermined weight of the starting powder was first pressed uniaxially at 12.6 MPa for 1 min using a 20-mm steel die, followed by cold isostatic pressing (CIP) at 70.4 MPa for 1 min. The resultant powder compact was sintered at 1400°C for 3 h in air.

The apparent density of the sintered body was measured by the Archimedes method. The relative density was calculated by comparing the apparent density to the theoretical one. The crystalline phases were identified by X-ray diffraction (XRD; Multiplex; Rigaku, Japan).

For both conductivity and temperature measurements, sintered bodies were cut into rectangular bars of dimensions 4 × 4 × 9 mm³ using a precision cutter. Electrodes were formed by painting gold paste on each 4 × 4 mm² side of a specimen, followed by heat treatment at 1100°C for 10 min. AC impedance measurements (Modulab XM; Solatron, UK) were then carried out on specimens heated either conventionally or by MMW irradiation. The measurements were conducted from 0.1 to 1 MHz and 400 to 1000°C at an oscillation voltage of 300 mV. Bulk conductivities (σᵦ) were obtained from Cole–Cole plots, which were qualitatively confirmed by fitting to the universal dielectric response (UDR).11

MMW heating is distinguished by a self-heating effect, which differs from conventional heating where temperature elevation occurs by heat transport from the ambient air and from the absorption of infrared radiation by the surface of a material. Heat
activation energy for ionic conduction $E$ depends on the transfer energy $E_m$ and the dissociation energy $E_o$. The total activation energy obtained from the Arrhenius plot at higher temperatures excludes $E_o$ because all of the associations between the positively charged vacancies and oxide ions were thought to have dissociated at higher temperature. When the change in activation energy, $\Delta E_m$ and $\Delta E_o$, were compared between conventional and MMW heating, the former was larger than the latter, suggesting that MMW irradiation had a greater influence on the transfer energy than the dissociation energy. The same behavior was found in our previous research.9,14)

Figure 3 shows the degree of conductivity enhancement at 400°C as a function of upper and lower susceptor thicknesses. The conductivity enhancement increased with decreasing upper susceptor thickness. If the conductivity depended only on the temperature, then a sample with a smaller temperature gradient would show greater conductivity. In the present case, samples with thinner upper susceptors had higher conductivities, although the low-temperature portion of the gradient was larger with thinner susceptors. The conductivity enhancement peaked for the 1–3 susceptor configuration. Multiple temperature measurements were performed to establish the temperature profile close to the samples.

We assumed that the center of a sample heated by MMW irradiation would have the maximum temperature. In our previous study where the conductivity was measured under MMW heating, a thermocouple had been inserted into the center of a sample to avoid underestimating the sample temperature. By using two additional points [Fig. 1(b)], the temperature profiles of samples
under MMW irradiation heating were measured as the thickness of each susceptor was changed.

**Figure 4** shows the results for the 2–3 susceptor case. For any combination of susceptors, the temperature difference between Ch 0 and Ch 1 was marginal, while that at Ch 2 was somewhat lower than the central temperature of 300°C. Since the sample under MMW irradiation had a lower temperature than that at the center or original monitoring point, any conductivity enhancement was attributed not to an underestimation of temperature but to some kind of non-thermal effect.

**Figure 5** shows the conductivity enhancement as a function of the temperature difference between Ch 0 and Ch 2 caused by changing the susceptor thickness. In the present study, the temperature difference ranged from −20 to −100°C. The conductivity enhancement increased when the absolute temperature difference increased from −20 to −60°C. The absolute temperature difference decreased with decreasing susceptor thickness. Since heat transport from the susceptors simultaneously decreased, the self-generated heat ratio of the samples should have increased to a predetermined temperature. For that temperature range, then, the conductivity enhancement increased with increasing self-generated heat.

The conductivity enhancement decreased when the absolute temperature difference increased further from −60°C. The self-generated heat ratio also increased over this temperature range, but the greater low-temperature portion should have influenced the total conductivity. In the present sample set-up, the conductivity enhancement under MMW irradiation heating peaked for a temperature difference of −60°C when the ratio of self-generated heat and the volume of the low-temperature portions were well balanced.

**Figure 6** illustrates the above-described heating conditions under MMW irradiation. In this arrangement, the change in temperature (increase, remain, or decrease) was determined by the subscription outflow rate from the sum of the inflow rate and the self-generated heating rate.

The MMW irradiation power should be increased to balance the heat outflow (radiation) and attain a steady high temperature. Without susceptors, heat outflow from the surface of the sample is considerable. Under these conditions, the temperature gradient between the center and the surface is large. Such a temperature gradient can be reduced by increasing the thickness of the susceptors to decrease the heat outflow as a result of increased heat generation of the susceptors. With a small temperature gradient, self-heat generation also becomes small because of the larger inflow of heat from the thicker susceptors. In other words, the temperature gradient of a sample is positively related to the self-generated heat.

As demonstrated by the temperature profile monitoring, the maximum temperature under MMW irradiation occurred at the center of a sample. The obtained conductivity enhancement did not result from an underestimation of the sample temperature. A non-thermal effect probably enhanced ion transport because oxide ion conductivity was improved even within the low-temperature portion of the sample.

According to the pondermotive model,15)16) which is a representative non-thermal effect under MMW irradiation, transport of charged species would be enhanced according to the power of electromagnetic field. The degree of ponderomotive force, depends on the absorption of MMW radiation. This absorption is directly related to the self-generated heat of a sample exposed to a specific MMW frequency.17) In the present case, the temperature gradient of a sample depended on the self-generated heat. The conductivity enhancement or ion transport would increase with increasing temperature gradient because of increasing ponderomotive force. A further increase in the temperature gradient increases the volume fraction of the low-temperature portion, leading to a decrease in the total conductivity.

### 4. Conclusions

The conductivity enhancement under MMW irradiation heating was examined by changing the thermal gradient of an 8YSZ sample. The enhancement increased with increasing temperature gradient. The maximum conductivity enhancement of up to 25-fold at 400°C with a temperature gradient of −60°C was attributed to a non-thermal effect. A further increase of the absolute temperature gradient led to a decrease in total conductivity enhancement, probably because of a larger low-temperature portion.

**Acknowledgement** This work was partially supported by JSPS KAKENHI (Grant Number: 16H04497).
References
1) T. J. Mazanec, Solid State Ionics, 70/71, 11–19 (1994).
2) S. Singhal, MRS Bull., 25, 16–21 (2000).
3) V. M. Janardhanan and O. Deutschmann, Z. Phys. Chem., 221, 443–478 (2007).
4) N. Shaigan, W. Qu, D. G. Ivey and W. Chen, J. Power Sources, 195, 1529–1542 (2010).
5) J. Patakangas, Y. Ma, Y. Jing and P. Lund, J. Power Sources, 263, 315–331 (2014).
6) S. P. S. Badwal and K. Forger, Ceram. Int., 22, 257–265 (1996).
7) S. Hui, J. Roller, S. Vick, X. Zhang, C. Deces-Petit, Y. Xie, R. Marie and D. Ghosh, J. Power Sources, 172, 493–502 (2007).
8) A. Kishimoto, K. Ayano and H. Hayashi, Scr. Mater., 64, 860–863 (2011).
9) A. Kishimoto, K. Ayano, T. Teranishi and H. Hayashi, Mater. Chem. Phys., 143, 486–489 (2014).
10) A. Kishimoto, H. Hasunuma, T. Teranishi and H. Hayashi, J. Alloy. Compd., 648, 740–744 (2015).
11) S. S. B. C. Abdullah, T. Teranishi, H. Hayashi and A. Kishimoto, J. Jpn. Soc. Powder Powder Metallurgy, 63, 663–667 (2016).
12) S. S. B. C. Abdullah, T. Teranishi, H. Hayashi and A. Kishimoto, Mater. Design, 115, 231–237 (2017).
13) A. K. Jonscher, Nature, 267, 673–679 (1997).
14) M. Filal, M. Mokchah, C. Chateau and J. L. Carpentier, Solid State Ionics, 80, 27–35 (1995).
15) K. I. Rybakov and V. E. Semenov, Phys. Rev. B, 49, 64–68 (1994).
16) K. L. Rybakov and V. E. Semenov, Phys. Rev. B, 52, 3030–3033 (1995).
17) B. Aissa, N. Tabet, M. Nedil, Therriault, F. Rosei and R. Nechache, Appl. Surf. Sci., 258, 5482–5485 (2012).