Calculating Method of Dielectric Permittivity of 8YSZ in Different Relative Humidity with Low Water Contents

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Abstract: An improved approach for calculating the dielectric permittivity of 8 mol% yttria-stabilized zirconia (8YSZ) in different relative humidity corresponding to low water contents is proposed. For this, a new virtual pore constituted by air and water is proposed using the microstructural modeling. 8YSZ material is assumed to be made up of 8YSZ solid and virtual pore. The results showed that the dielectric permittivity of the virtual pore is calculated using the upper limit of the Wiener approach for low water contents, and the effective dielectric permittivity of 8YSZ material constituted by solid and virtual pore in different relative humidity using Jayannavar’s expression. The proposed approach gives a better interpretation of the experimental results in different relative humidity corresponding to low water contents.

Keywords: 8YSZ, microstructure, dielectric permittivity, relative humidity

1. Introduction

8mol% yttria-stabilized zirconia (8YSZ) has been used in various fields including thermal barrier coatings [1-3], oxygen sensors [4,5], solid oxide fuel cells [6,7] and biocompatible implant coatings [8,9].

Investigations have been made on the various properties of 8YSZ treated at different temperatures [10-12].

When 8YSZ is placed in different relative humidity, its dielectric permittivity can vary with the microstructure of material and the relative humidity.

For the past few years, the calculation of the physical properties of 8YSZ in different relative humidity has been studied by Nait-Ali et al. [13,14]. Their approach for calculating the dielectric permittivity of 8YSZ gives a good interpretation of the experimental results for high water contents, but it causes the deviation between the experimental value and the calculation for low water contents.

This work deals with the calculation of the dielectric permittivity of 8YSZ in different relative humidity corresponding to low water contents in more detail.

2. Approach proposed by Zouaoui et al.

In 2016, Zouaoui et al. reported an approach for calculating the dielectric permittivity of 8YSZ in different humidity using microstructural modeling [13].

The main idea of microstructural modeling is that a three-phase system constitutes by solid, air and water can be considered to be a two-phase system by the solid and virtual pore.

Until now, a number of methods have been proposed to calculate the dielectric permittivity of two-phase composites.

For this reason, the main study on calculation of the dielectric permittivity of 8YSZ in different relative humidity was focused on converting the practical material to a two-phase system.

In 2013, Nait-Ali et al. proposed a new microstructural modeling for calculating the thermal conductivity of 8YSZ in different relative humidity [14].

Considering 8YSZ in different relative humidity is a three-phase material containing solid, air and water, they converted the three-phase material to two-phase using the conception of a virtual pore. This virtual pore is a spherical pore that a water layer is located at the interface between the internal solid surface and the air.

Therefore, 8YSZ can be considered as a two-phase material, which consists of solid and virtual pores. With this model, they calculated the dielectric permittivity of the virtual pore using the upper limit of the Hashin-Shtrikman approach [15], as follows:

\[ \varepsilon_{vp} = \varepsilon_{water} + \frac{\phi_{air} \varepsilon_{air}}{1 + \phi_{water} \varepsilon_{water}} \]

(1)

where \( \varepsilon_{vp} \) is the dielectric permittivity of the virtual pore, \( \varepsilon_{air}, \phi_{air} \), \( \varepsilon_{water}, \phi_{water} \) are the dielectric permittivity and the volume fraction of air and water, respectively.

Finally, they calculated the effective permittivity of 8YSZ by taking into account the Jayannavar’s expression [16], as follows:

\[ \varepsilon_{eff} = \varepsilon_{solid} + \frac{1}{4} \left[ \begin{array}{c} \varepsilon_{water}(3\phi_{air} - 1) + \varepsilon_{air}(3\phi_{water} - 1) + \varepsilon_{air}(3\phi_{water} - 1) \varepsilon_{water}(3\phi_{air} - 1) \varepsilon_{solid}(3\phi_{air} - 1) \varepsilon_{air}(3\phi_{water} - 1) \varepsilon_{water}(3\phi_{air} - 1) \varepsilon_{air}(3\phi_{water} - 1) \end{array} \right] \]

(2)

where \( \varepsilon_{solid}, \phi_{solid} \) and \( \varepsilon_{vp}, \phi_{vp} \) are the dielectric permittivity and the volume fraction of 8YSZ solid and the virtual pore, respectively.

They compared the experimental values with calculations, and then explained the validity of the proposed approach. On the other hand, they pointed out their approach is undesirable when the water content is not enough to cover the internal solid surface with a single water molecular layer.

The above approach for calculating the dielectric permittivity gives a good interpretation of the experimental results for high water contents, but it causes the deviation between the experimental value and the calculation for low water contents.
3. Proposed approach

According to the Zouaoui’s approach, the water content in 8YSZ is enough to cover the internal solid surface at a given relative humidity. The Zouaoui’s approach does not necessarily apply to all cases, because the low water content is not enough to cover the internal solid surface of 8YSZ.

Hence, it is necessary to consider the calculation of the dielectric permittivity of 8YSZ in different relative humidity.

Here, the essential question is to propose the most suitable virtual pore constituted by water and air that can reflect the microstructure of 8YSZ sufficiently for low water contents.

To solve this problem, we assume that spherical water droplets are randomly located in the neck regions formed by grains and surrounded by the pores. In other words, this implies 8YSZ is a two-phase material constituted by the solid region and the virtual pore region where the water droplets are penetrated in the pores, randomly.

Fig. 1 shows our microstructural modeling to calculate the dielectric permittivity of 8YSZ for low water contents.

![Fig.1. The equivalent microstructure corresponding to 8YSZ for low water contents](image)

There are various approaches for calculating the dielectric permittivity of two-phase material.

The Wiener approach has often been used to evaluate the dielectric permittivity of two-phase composites, in the following ex

\[
E_{water} = \phi_1 \varepsilon_1 + \phi_2 \varepsilon_2
\]

\[
E_{upper} = \phi_1 \varepsilon_1 + \phi_2 \varepsilon_2
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric permittivity of phase 1 and phase 2, respectively, \( \phi_1 \) and \( \phi_2 \) are the volume fractions corresponding to these phases, respectively. \( E_{upper} \) and \( E_{lower} \) are the upper and lower limits of the effective permittivity of the two-phase material, respectively.

In addition, there are various approaches for calculating the dielectric permittivity of a two-phase material including the Bruggeman approach [18] (Eq. (5)) and the Maxwell Garnet approach [19] (Eq. (6)).

\[
E = E_1 \left( \frac{3 \varepsilon_1 + 2 \phi \left( \varepsilon_1 - \varepsilon_2 \right)}{3 \varepsilon_1 - \phi \left( \varepsilon_1 - \varepsilon_2 \right)} \right)
\]

\[
E = E_1 + 3 \phi E_1 \left( \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + 2 \varepsilon_1 - \phi \left( \varepsilon_2 - \varepsilon_1 \right)} \right)
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric permittivity of phase 1 and phase 2, respectively, \( E \) is the effective permittivity of two-phase material, and \( \phi \) is the volume fraction of phase 1.

From among the approaches mentioned above, a suitable approach was chosen.

For low water contents, an analytical trial of the dielectric permittivity of the virtual pore was made by using the above mentioned equations in combination with Eq.2 and we found the upper limit of the Wiener approach gives a good interpretation of the experimental results.

Consequently, when the water content in 8YSZ is not enough to cover the surface of solid, we found that the dielectric permittivity of the virtual pore can be approximated by the upper limit of the Wiener approach.

From Eq. (3), the dielectric permittivity of the virtual pore is given by:

\[
E_{vp} = \phi_{air} E_{air} + \phi_{water} E_{water}
\]

where \( E_{vp} \) is the dielectric permittivity of the virtual pore; and \( (\phi_{air}, E_{air}), (\phi_{water}, E_{water}) \) are the dielectric permittivity and the volume fraction of air and water, respectively.

The water content in the 8YSZ is calculated using the following equation:

\[
x_{water} = \frac{m_{humid} - m_{dry}}{m_{humid}}
\]

where \( x_{water} \) is the water content in the sample; and \( m_{humid}, m_{dry} \) are the weights of the sample containing the water and the dried sample, respectively.

For calculation, Eq. (8) can be expressed as:

\[
\phi_{water} = \rho_{dry} \left( \frac{1}{1 - x_{water}} - 1 \right)
\]

where \( \phi_{water} \) is the volume fraction of water in the sample and \( \rho_{dry} \) is the bulk density of the dried sample.

Using Eq. (9) and Eq. (7), \( E_{vp} \) can be expressed as :

\[
E_{vp} = E_{air} + \rho_{dry} x_{water} \frac{E_{water} - E_{air}}{1 - x_{water}}
\]

The effective dielectric permittivity of 8YSZ constituted by the solid and the virtual pore is calculated using Eq. (2) using the Jayannavar’s expression.

Therefore, the effective dielectric permittivity of 8YSZ can be calculated by using Eq. (10) and Eq. (2) for low water contents.

However, when the water content is enough to cover the surface of solid, the permittivity of the virtual pore is calculated using the upper limit of Hashin-Shtrikman approach (Eq. (1)).

Consequently, the dielectric permittivity of the virtual pore is calculated using the upper limit of the Wiener approach for low water contents and the upper limit of Hashin-Shtrikman approach for high water contents.

4. Validation of the proposed approach

Using the proposed approach, the dielectric permittivity for four 8YSZ samples in different relative humidity from <3% to 100% were calculated.

The experimental data at room temperature reported by Nait-Ali et al. were used for evaluating the dielectric permittivity of
The 8YSZ samples are cylindrical with a thickness of 1 mm and a diameter of 13 mm. Heat treatment temperatures are 400°C, 800°C, and 1 000°C, respectively: the maintaining time is 1 h; and the heating rate is 5°C min⁻¹.

The physical properties such as specific surface area and pore volume fraction vary with the heat treatment temperature. The dielectric permittivity of 8YSZ solid phase, air, and water are 30±1 [20], 1, and 80, respectively.

Table 1 shows the physical properties of the 8YSZ samples treated thermally at different temperatures. The data of the pore volume fraction and the water content from Table 2 to Table 5 are the arithmetical averages of the measured data reported by Ref. [13] and Ref. [14] under the same conditions, respectively.

### Table 1. Physical properties of 8YSZ samples treated at different temperature

| Sample ref. | Heat treatment temperature (°C) | Bulk density (g/cm³) | Pore volume fraction (%) | Specific surface area (㎡/g) |
|-------------|---------------------------------|----------------------|--------------------------|-----------------------------|
| A           | No thermal treatment            | 2.66                 | 55.45                    | 170                         |
| B           | 400                             | 2.80                 | 52.75                    | 123                         |
| C           | 800                             | 3.24                 | 48.65                    | 53                          |
| D           | 1000                            | 4.23                 | 31.4                     | 12                          |

### 4.1. Untreated 8YSZ (sample A)

Table 2 shows the water contents and the number of water layers of sample A in different relative humidity.

### Table 2. Water content and number of water layers on the surface of 8YSZ untreated in different relative humidity

| Relative humidity (%) | Water content (%) | Number of water layer on the surface |
|-----------------------|-------------------|-------------------------------------|
| <3                    | 0.8               | 0.20                                |
| 11                    | 3.1               | 0.65                                |
| 43                    | 5.0               | 1.10                                |
| 75                    | 10.2              | 1.40                                |
| 85                    | 13.4              | 3.20                                |
| >99                   | 14.3              | 3.61                                |

Fig. 2 shows the comparison between the calculations and the experimental data for sample A.

### 4.2. 8YSZ treated at 400°C (sample B)

Table 3 shows the water contents and the number of water layers of sample B in different relative humidity. Fig. 3 shows the comparison between the calculations and the experimental data for sample B.

### Table 3. Water content and number of water layers on the surface of 8YSZ treated at 400°C in different relative humidity

| Relative humidity (%) | Water content (%) | Number of water layer on the surface |
|-----------------------|-------------------|-------------------------------------|
| <3                    | 1.0               | 0.25                                |
| 11                    | 2.2               | 0.75                                |
| 43                    | 3.4               | 1.15                                |
| 75                    | 8.7               | 2.70                                |
| 85                    | 12.0              | 3.95                                |
| >99                   | 12.6              | 4.40                                |

Fig. 3. Water content dependence of the dielectric permittivity for sample B.

### 4.3. 8YSZ treated at 800°C (sample C)

Table 4 shows the water contents and the number of water layers of sample C in different relative humidity. Fig. 4 shows the comparison between the calculations and the experimental data for sample C.

### Table 4. Water content and number of water layers on the surface of 8YSZ treated at 800°C in different relative humidity

| Relative humidity (%) | Water content (%) | Number of water layer on the surface |
|-----------------------|-------------------|-------------------------------------|
| <3                    | 0.6               | 0.35                                |
| 11                    | 1.0               | 0.70                                |
| 43                    | 1.5               | 1.00                                |
| 75                    | 2.1               | 1.50                                |
| 85                    | 4.5               | 3.25                                |
| >99                   | 10.2              | 8.10                                |

Fig. 4. Water content dependence of the dielectric permittivity for sample C.
layers of sample C in different relative humidity.

Fig. 4 shows the comparison between the calculations and the experimental data for sample C.

### 4.4. 8YSZ treated at 1 000 °C (sample D)

Table 5 shows the water contents and the number of water layers of sample D in different relative humidity.

| Relative humidity (%) | Water content (%) | Number of water layer on the surface |
|-----------------------|-------------------|-------------------------------------|
| <3                    | 0.2               | 0.45                                |
| 11                    | 0.3               | 0.80                                |
| 43                    | 0.4               | 1.00                                |
| 75                    | 0.4               | 1.20                                |
| 85                    | 0.5               | 1.45                                |
| >99                   | 3.9               | 14.05                               |

Fig. 5 shows the comparison between the calculations and the experimental data for sample D.

![Comparison between calculations and experimental data for sample D](image)

**Fig. 5. Water content dependence of the dielectric permittivity for sample D.**

### 5. Discussion

For all cases, when the numbers of water layers on the surface of 8YSZ are less than 1.5, the proposed approach gives a better interpretation of the experimental results than the Zouaoui’s approach. In contrast, when the numbers of water layers on the surface of 8YSZ are more than 1.5, the Zouaoui’s approach gives a better interpretation of the experimental results than the proposed approach. On the other hand, this shows that when the theoretical value of the number of water layers on 8YSZ surface is 1, the water content is not enough to cover the internal solid surface completely.

Accordingly, the dielectric permittivity of 8YSZ in different relative humidity can be calculated using either of the two approaches by taking into account the number of the water layers on the solid surface.

In particular, the 8YSZ treated at high temperature (> 1 000°C) has the number of water layers less than 1.5 in different relative humidity between 3% and 85%, and as a result, the dielectric permittivity can be calculated by using the proposed approach under normal condition.

However, when the number of water layers on the surface is more than 1.5, the proposed approach causes strong deviation between the experimental results and the calculations, and in contrast, the Zouaoui’s approach gives a better interpretation of the experimental results. On the other hand, this shows that when the theoretical value of the number of water layer is more than 1.5, the water content is enough to cover the internal solid surface completely.

The results of the proposed approach confirm not only the accuracy of the experiment by Nait-Ali et al. but also the validity of their approach for high water contents.

### 6. Conclusion

The dielectric permittivity of 8YSZ in different relative humidity can be calculated by taking into account the water content in material. The proposed approach is based on the conversion of three-phase system to two-phase system. For a relative humidity corresponding to the number of water layers less than 1.5, the microstructural modeling is based on the assumption that the system is made up the solid region and the virtual pore region where the water droplets are penetrated in the pores randomly. For a relative humidity corresponding to the number of water layers more than 1.5, the microstructural modeling is based on the approach proposed by Nait-Ali et al.

The dielectric permittivity of the virtual pore is corresponded to the upper limit of the Wiener approach for low water contents, and the upper limit of the Hashin-Shtrikman approach for high water contents. The effective dielectric permittivity of a two-phase material constituted by the solid phase and the virtual pore is calculated using Jayannavar’s expression.

Experimental results agree closely with calculations made with the proposed approach for a relative humidity corresponding to the number of water layers less than 1.5.

However, for a relative humidity corresponding to the number of water layers more than 1.5, it is appropriate to calculate the dielectric permittivity using the approach by Zouaoui et al.

### Conflict of Interest

No conflict of interest exists. We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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