

Effect of zirconia content on electrical conductivities of mullite/zirconia composites measured by impedance spectroscopy

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Electrical conductivities of various mullite/zirconia composites, as well as monolithic mullite and zirconia, were measured using AC impedance spectroscopy from 100 Hz to 10 MHz at temperatures ranging from 150 to 1300 °C. The impedance spectra of monolithic zirconia and mullite/zirconia composites showed two semicircles because of the contributions from grains and grain boundaries, while those of monolithic mullite had one semicircle due to the predominant contribution from grains. This indicates that the conductivities of the mullite/zirconia composites increased with zirconia content. The activation energies of electrical conduction in mullite and zirconia were about 65 and 79 kJ/mol, respectively, and those of mullite/zirconia composites were between 65 and 79 kJ/mol. While the conductivities of various composites at 1 MHz were fitted by Lichtenecker's rule, the general mixing equation could be applied to the conductivities measured at 1 kHz.

I. INTRODUCTION

Although mullite has good high-temperature strength and chemical stability, its low toughness limits its use in advanced structural applications. The mechanical properties of PSZ/mullite, SiCw/mullite, and SiCw/PSZ/mullite composites have been studied by many investigators.^{1–5} It is well known that partially stabilized zirconia (PSZ) and/or SiC whiskers can significantly improve the mechanical properties of mullite via mechanisms such as phase transformation toughening, whisker bridging, and crack deflection.

As far as electric properties are concerned, mullite is a good insulator at room temperature and can be considered a semiconductor at high temperatures.^{6,7} Gerhardt and Ruh⁸ reported that the incorporation of SiC whiskers significantly affected the electrical properties of mullite matrix composites because SiC has a large dielectric constant (42 for SiC and 6.5 for mullite at 1 MHz)⁹ and a small electric resistivity (5×10^5 ohm-cm for SiC and 1×10^{13} ohm-cm for mullite at room temperature)^{10,11} with respect to mullite. Previous studies have also been conducted on other composites.^{12,13} Gerhardt¹² showed the

influence of volume fraction, size, and shape of reinforcing agents on the electrical properties of ceramic matrix and polymer matrix composites. Runyan et al.¹³ studied the electrical conductivities of BN–B₄C and BN–SiC composites under different orientations of the applied electrical field, and the results were fit by the McLachlan equation or general effective medium equation. It is believed that the dramatic change in electrical properties with respect to the volume fraction is attributable to the formation of interconnected channels of the good conducting phase within the composites.

For electrochemical applications, mullite and zirconia can be used as the solid electrolyte of an oxygen concentration cell because oxygen ions can transport through oxygen vacancies.^{14–16} Since the physical and/or chemical properties of composite materials could be tailored by incorporating various amounts of a second phase into a suitable matrix, a mullite/zirconia composite should be considered as a potential solid electrolyte at elevated temperatures as well. The properties of composites, however, could be dependent on the intrinsic nature and the volume fractions of their constituents. Because there is a lack of literature on the subject, it is desirable to have a measurement of the electrical properties of mullite/zirconia composites. Therefore, the effect of zirconia content on the electric conductivities is elucidated in this study.

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II. EXPERIMENTAL PROCEDURE

The raw materials used in this study were commercial mullite powder (with a nominal composition 71.86 wt% Al_2O_3 , 28.07 wt% SiO_2 , 0.03 wt% Fe_2O_3 , 0.03 wt% Na_2O , and 0.01 wt% MgO ; KM-mullite, Kyoritsu Ceramic Materials Co., Nagoya, Japan) and 3 mol% Y_2O_3 partially stabilized zirconia powder (3Y-PSZ, with a nominal composition 94.75 wt% ZrO_2 , 5.21 wt% Y_2O_3 , 0.005 wt% Al_2O_3 , 0.005 wt% SiO_2 , 0.002 wt% Fe_2O_3 , and 0.022 wt% Na_2O ; TZ-3Y, Toyo Soda Mfg., Co., Tokyo, Japan).

The zirconia content in the mullite/zirconia composites was in the range from 5 to 80 vol%. The sample containing 5 vol% 3Y-PSZ was designated MZY05. Others were designated in a similar way with "M" and "Z" standing for monolithic mullite and 3Y-PSZ, respectively. The designations, compositions, hot pressing conditions, and relative densities of various composites are listed in Table I.

Experimental samples were fabricated by hot pressing at a temperature of 1675 °C for pure mullite and at 1600 °C for mullite/zirconia composites in argon at a pressure of 30 MPa for 45 min (Model HP50-HTG-7010, Thermal Technology Inc., Santa Rosa, CA). After hot pressing, the zirconia in the composites became oxygen deficient and blackened. The hot-pressed composites and zirconia were then annealed at 1360 °C/4 h in air so that near-stoichiometric zirconia was obtained. Bulk densities were measured by the Archimedes method using deionized water as an immersion medium. The phases in each composite were identified using an x-ray diffractometer (XRD; Model MXP18, Mac Science, Yokohama, Japan). The measuring conditions of the XRD were Cu $\text{K}\alpha$ radiation at 50 kV, 150 mA, and a scanning rate of 2°/min. The zirconia contained both monoclinic and tetragonal phases in all composites as shown in Table I.

Microstructures were characterized by a scanning electron microscope (SEM; Model JSM-6500, JEOL, Tokyo, Japan). The SEM specimens were cut into pieces

about $5 \times 6 \times 0.5$ mm, ground, and polished with diamond paste using standard procedures.

The Pt paste diluted with alcohol was painted on the surface of each sample and fired at 1000 °C/10 min to prepare the electrode. Then, the sample was placed on a Pt plate. Two Pt wires were used to connect the sample to the measuring system; one contacted to the Pt electrode and the other to the Pt plate. The conductivity measurements were carried out by an alternating current (ac) impedance spectroscopy (Model 4194A, Hewlett Packard Co., Palo Alto, CA) in the frequency range of 100 Hz to 10 MHz at temperatures between 150 and 1300 °C in air. The impedance-measuring system is schematically shown in Fig. 1. The impedance data were analyzed and fitted using the electrochemical impedance software, Z-view.¹⁷

III. RESULTS AND DISCUSSION

A. Analyses of impedance spectra

The impedances of mullite and low-zirconia composites were found to be extremely large and scattered with significant errors at $T \leq 300$ °C. Their impedances were large enough so that the effect of inductive reactance was negligible. In the other respect, the impedance data of zirconia and high-zirconia composites at high temperatures were not adopted due to the inductive reactance. The Pt electrodes painted on the samples were porous and therefore could be regarded as several small metal wires. The electric current through the porous Pt electrode induced the inductive reactance, which adversely affected the conductivity measurements of zirconia and high-zirconia composites. Some of the measured impedance data in the high-frequency impedance spectra of zirconia and high-zirconia composites have a positive reactance. These data were unable to be analyzed, and it was noted that the degree of deviation from negative values increased with temperature. At high temperatures, zirconia behaves like a fast ion conductor, and the effect

TABLE I. Designations, compositions, hot pressing conditions, relative densities, and x-ray phases of various mullite/ ZrO_2 composites.

Designation	Composition ^a	Hot pressing condition ^b	Relative density (%)	XRD phases ^a
M	100 vol% M	1675 °C/45 min	97.8	M
MZY05	95 vol% M + 5 vol% Z	1600 °C/45 min	97.1	M, <i>t</i> -Z, <i>m</i> -Z
MZY10	90 vol% M + 10 vol% Z	1600 °C/45 min	96.7	M, <i>t</i> -Z, <i>m</i> -Z
MZY20	80 vol% M + 20 vol% Z	1600 °C/45 min	95.4	M, <i>t</i> -Z, <i>m</i> -Z
MZY30	70 vol% M + 30 vol% Z	1600 °C/45 min	96.7	M, <i>t</i> -Z, <i>m</i> -Z
MZY40	60 vol% M + 40 vol% Z	1600 °C/45 min	97.5	M, <i>t</i> -Z, <i>m</i> -Z
MZY50	50 vol% M + 50 vol% Z	1600 °C/45 min	97.1	M, <i>t</i> -Z, <i>m</i> -Z
MZY60	40 vol% M + 60 vol% Z	1600 °C/45 min	97.8	M, <i>t</i> -Z, <i>m</i> -Z
MZY80	20 vol% M + 80 vol% Z	1600 °C/45 min	97.7	M, <i>t</i> -Z, <i>m</i> -Z
Z	100 vol% Z	1600 °C/45 min	99.9	<i>t</i> -Z, <i>m</i> -Z

^aM, mullite; Z, 3 mol% Y_2O_3 - ZrO_2 ; *t*-Z, tetragonal ZrO_2 ; *m*-Z, monoclinic ZrO_2 .

^bAll samples were fabricated under the pressure of 30 MPa in Ar.

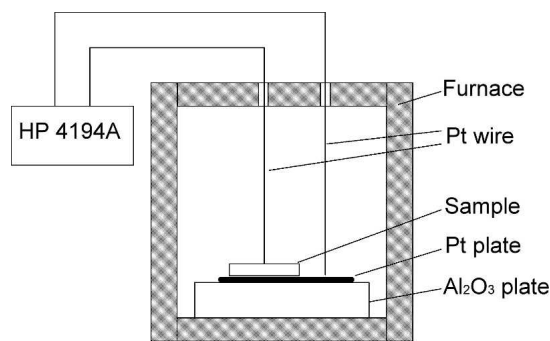


FIG. 1. Impedance-measuring system.

of inductive reactance becomes more apparent. Thus, one could not accurately obtain their electrical properties from the data measured at high frequencies and high temperatures.

Figure 2(a) shows the typical impedance spectra for MZY10 at temperatures ranging from 400 to 1000 °C. The horizontal axis is the real part of impedance (or resistance), while the vertical axis is the corresponding imaginary part (or reactance). The frequencies increased from right to left along the horizontal axis. The shape of the impedance spectra for MZY10 did not change significantly with respect to temperature, but the overall values of impedance did sharply decrease with temperature. Figure 2(b) shows the impedance spectra for MZY80 at temperatures between 200 and 450 °C, with two distinct semicircles in each impedance spectrum. The two semicircles corresponding to high and low frequencies in the impedance spectra of MZY80 were related to grains and grain boundaries, respectively.^{18,19} The resistivities of MZY10 and MZY80 decreased with increasing temperature in the same way exhibited by the general ceramics. This is caused by the so-called negative temperature coefficient (NTC) behavior.

Figure 3 shows the impedance spectra of the composites with various zirconia contents at fixed temperatures. Note that the resistivities decrease with increasing zirconia content because zirconia, which is known to be a good ionic conductor, has a much smaller resistivity than mullite. Figure 3(a) shows only one semicircle in the impedance spectrum of monolithic mullite at 700 °C. Monolithic mullite shows similar behavior, as reported in pervious studies.^{20,21} The relaxation frequencies for mullite were estimated to be between 20 kHz and 1 MHz at temperatures ranging from 500 to 1300 °C. The semicircle in the impedance spectra of mullite could be caused by the predominant contribution of grains because of the high relaxation frequency values.²¹

Meng and Huggins²² indicated that oxygen ionic conduction could be expected in mullite when oxygen vacancies were created by the substitution of Al^{3+} for Si^{4+} in the sillimanite structure. Hirata et al.²³ reported that the electrons in mullite could be excited to the conduc-

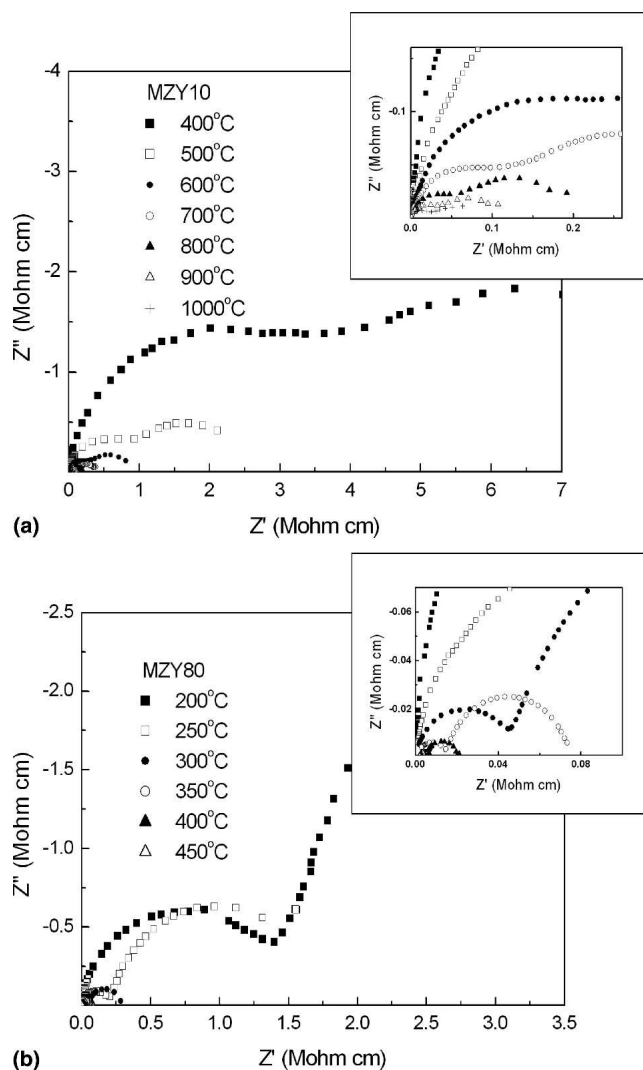
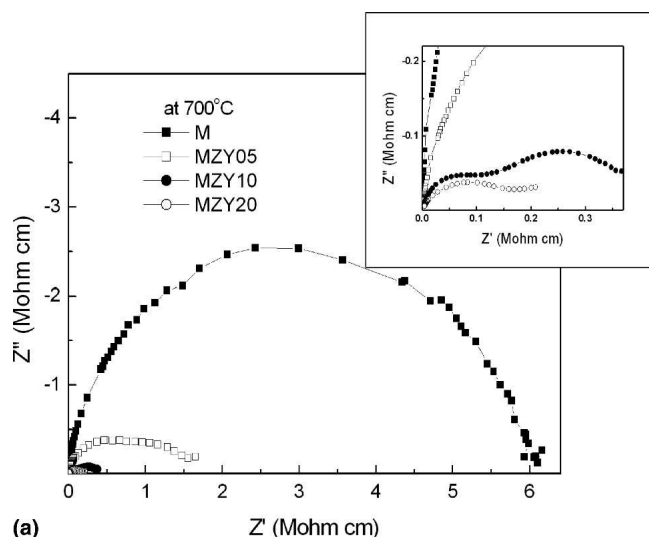


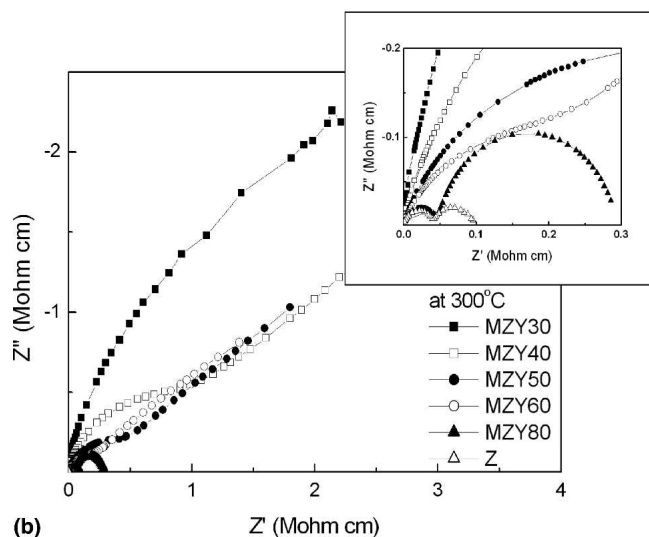
FIG. 2. Typical impedance spectra. (a) For MZY10 at temperatures ranging from 400 to 1000 °C. (b) For MZY80 at temperatures ranging from 200 to 450 °C. The enlarged views at low impedances are shown in the inset.

tion band at a low oxygen pressure and that the electrical conduction of mullite is a combination of electronic and ionic conduction in a nitrogen atmosphere. In this study, the electrical conduction in mullite should be ionic conduction since the measurements were conducted in air.

The impedance spectra of monolithic zirconia and MZY80, as shown in Fig. 3(b), clearly revealed two semicircles that were related to grains and grain boundaries of zirconia. The impedance spectra of mullite/zirconia composites other than MZY80, however, were unlike those of monolithic mullite and zirconia, as shown in Figs. 3(a) and 3(b). The impedance responses at high and low frequencies showed two partially overlapped semicircles. Note that the low- and high-frequency arcs in impedance spectra were gradually discernible as the ZrO_2 content was increased.



(a)



(b)

FIG. 3. Impedance spectra of the composites with various zirconia content. (a) M, MZY05, MZY10, and MZY20 at 700 °C. (b) MZY30, MZY40, MZY50, MZY60, MZY80, and Z at 300 °C. The enlarged views at low impedances are shown in the inset.

B. Conductivities and activation energies

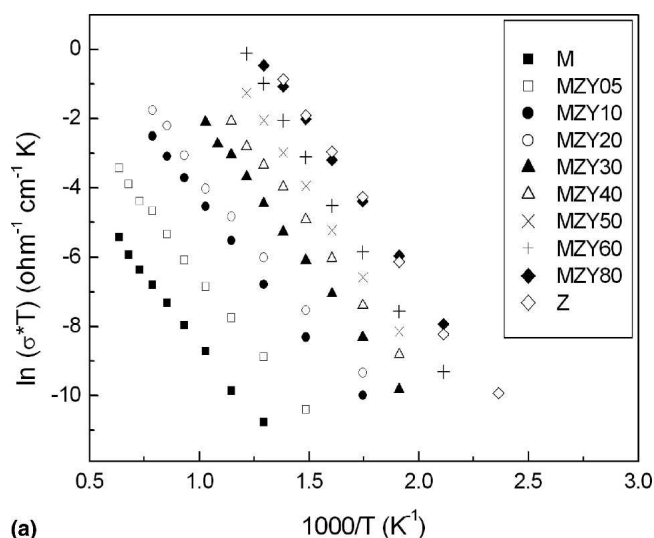
The impedance data of zirconia and zirconia/mullite composites can be divided into two semicircles corresponding to high and low frequencies. They were modeled by an equivalent circuit consisting of two R-CPE parallel circuits in series, where R and CPE are the resistor and the constant-phase element, respectively.²⁴ The impedance spectra of monolithic mullite showed, however, a single imperfect semicircle (i.e., a depressed circular arc), and its data were fit using a model of one R-CPE parallel circuit.²⁴ In the other way, the impedance spectra with a perfect semicircle would be fit by the equivalent circuit of one RC parallel circuit.

The conductivities of various composites obey the Arrhenius equation and can be expressed by:

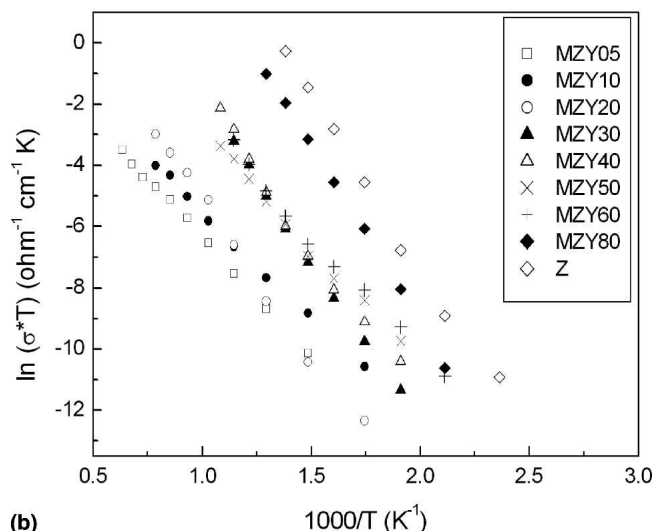
$$\sigma T = A \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where σ is the conductivity ($\text{ohm}^{-1} \text{cm}^{-1}$), A is a constant, E_a is the activation energy (kJ/mol), R is the gas constant ($\text{J/mol}\cdot\text{K}$), and T is the temperature (K).

Figure 4 displays the Arrhenius plots of $\ln(\sigma T)$ as a function of $1/T$ for all samples. The conductivities of the composites in the high-frequency region increased with increasing zirconia content as shown in Fig. 4(a). In contrast, the plots in Fig. 4(b) indicate that the conductivities in the low-frequency region exhibited a somewhat different trend. The conductivities of MZY20 at low temperatures were smaller than those of MZY05 and MZY10. Furthermore, the slope of the $\ln(\sigma T)$ versus $1/T$ curve for MZY20 was much larger than those for MZY05 and MZY10. The electrical conductivity versus



(a)



(b)

FIG. 4. Arrhenius plots of conductivities determined (a) in the high-frequency region; (b) in the low-frequency region of impedance spectra.

1/*T* curves of MZY30, MZY40, or MZY50 demonstrate a similar slope.

It was also noted that the conductivity in the high-frequency region (related to grains) of MZY80 was the same as that of zirconia, while the conductivity in the low-frequency region (related to grain boundaries) was much lower than that of zirconia. This can be explained by the fact that mullite grains are located at the grain boundaries of zirconia and the existence of intergranular mullite slightly decreased the conductivity of MZY80 along the grain boundaries. The intergranular mullite, however, did not affect the conductivity across the dense interconnected channels of zirconia grains in MZY80.

Figure 5 displays the activation energies of electrical conduction with respect to zirconia content in the high- and low-frequency regions. The activation energy for mullite was found to be about 65 kJ/mol, which is in agreement with previous studies.^{20,22} For zirconia, the activation energies of the grain conductivity at high frequencies and of the grain-boundary conductivity at low frequencies were found to be about 79 and 93 kJ/mol, respectively, agreeing with the results reported by Guo and Zhang.¹⁹

The activation energies in the high- and low-frequency regions for MZY05 and MZY10 are approximately the same as that for mullite. The high-frequency measurements of MZY05 and MZY10 could be correlated with the presence of grains of mullite. The grain conductivities of MZY05 and MZY10, however, were different from those of monolithic mullite. Zirconia has a much lower resistivity than mullite and can affect the electrical response in MZY05 and MZY10. That is why the grain conductivities for MZY05 and MZY10 are so different from those for monolithic mullite.

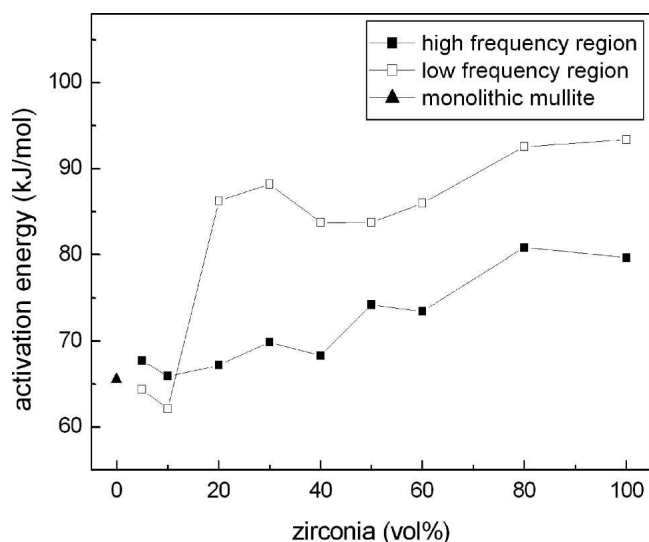


FIG. 5. The activation energy versus zirconia content curves of mullite/zirconia composites in the high-frequency and low-frequency regions, respectively, of the impedance spectra.

In contrast, the low-frequency regions for MZY05 and MZY10 were correlated to the grain boundaries of zirconia and/or mullite. While a glassy phase was usually observed in the grain boundaries of monolithic mullite, the composites containing zirconia were lacking a glassy phase.^{25,26} For MZY05 and MZY10, the low-frequency signal would transport through grain boundaries of mullite and/or zirconia instead of the glassy phase.

When the zirconia content was larger than 20 vol%, the activation energies in the low-frequency region were much higher than those of MZY05 and MZY10. This could be explained by the formation of a space charge layer at the interface of mullite and zirconia grains in an electric field. The space charge layer is usually formed at the interface of two phases with dissimilar electrical properties. The presence of a space charge potential would increase the activation energy of the electric conduction through the grain boundaries.¹⁹ Therefore, the low-frequency arcs of the composites were related to the space charge contribution when the zirconia content was larger than 20 vol%. There was not much difference in the activation energies from MZY20 to MZY60 at low frequencies. In contrast, the activation energies of the electric conduction in the high-frequency region between MZY20 and MZY60 increased gradually with zirconia content.

Figure 5 also shows that the activation energies of the electric conduction for MZY80 were close to those values for zirconia in the corresponding high- and low-frequency regions.

C. Conductivity versus zirconia content

Various theories describe the physical properties of a multiphase system. The general mixing equation is frequently used to predict the electrical properties of a heterogeneous system and can be expressed by²⁷:

$$\sigma_c^n = (1 - V) \sigma_m^n + V \sigma_z^n, \quad (2)$$

where *V* is the volume fraction of zirconia, σ_m , σ_z , and σ_c are the conductivities of mullite, zirconia, and composite, respectively, and *n* is a constant between −1 and 1. For the extreme, case, *n* = 1 if these two phases are laminated and laid parallel to the direction of electric current; *n* = −1 if these two phases are laminated and laid perpendicular to the direction of electric current. There is a mixed case where −1 < *n* < 1. When *n* → 0, the mixing equation is given by²⁷:

$$\log \sigma_c = (1 - V) \log \sigma_m + V \log \sigma_z. \quad (3)$$

This expression was first proposed by Lichtenecker and was called Lichtenecker's rule.²⁸ The empirical Lichtenecker's rule was applied successfully to estimate the dielectric content of a two-phase system in previous

studies.^{29,30} Zakri et al.³¹ demonstrated that Lichtenecker's rule is not only an empirical relationship based on experimental results, but also a theoretical model that can be derived from the effective medium theory.

To understand the change of electrical properties in composites with various zirconia contents, the resistance (R) of those samples was measured at some fixed low and high frequencies. Then, the conductivity (σ) was calculated using:

$$\sigma = \frac{1}{R} \cdot \frac{l}{A}, \quad (4)$$

where l and A are the thickness and cross-sectional area of the sample perpendicular to the electric current direction, respectively.

Figures 6(a) and 6(b) display the real parts of conduc-

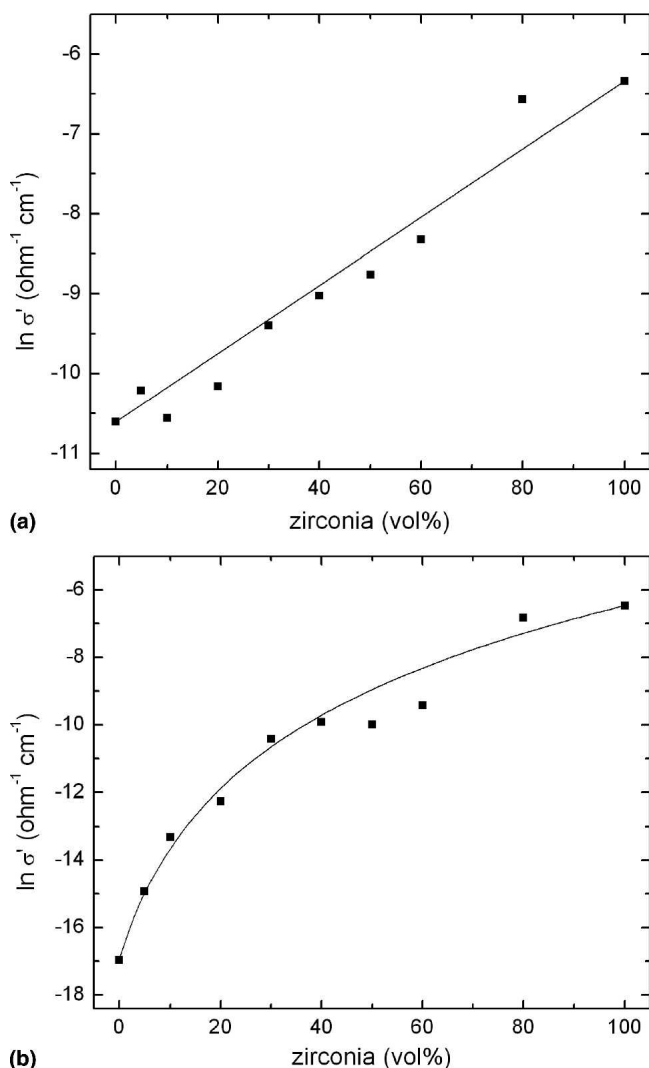


FIG. 6. The real part of conductivity versus zirconia content curve at the frequencies of (a) 1 MHz and (b) 1 kHz at 600 °C. The fitting lines in (a) and (b) were determined by Lichtenecker's rule and the general mixing equation, respectively.

tivity (σ') as a function of zirconia content at the frequencies of 1 kHz and 1 MHz, respectively, at 600 °C, indicating that the real part of conductivity increases with zirconia content. It was noted that the plot of $\ln \sigma'$ versus zirconia content at 1 MHz [Fig. 6(a)] demonstrates a linear behavior in agreement with Lichtenecker's rule. Figure 6(b), however, shows that the conductivities measured at 1 kHz with various zirconia contents were fit using the mixing rule [Eq. (2)]. The parameter n was about 0.25.

The different trends for the $\ln \sigma'$ of composites with various zirconia contents at 1 MHz and 1 kHz were caused by different factors. The conductivities measured at 1 MHz and 1 kHz were gained from the contribution of grains and grain boundaries, respectively. Figure 6(b) shows that the conductivities of composites with 30 to 60 vol% zirconia were not much different from the conductivities measured at 1 kHz. This could result from the existence of space charge at grain boundaries as mentioned previously. Though the space charge layer could deplete the charge carriers and cause an increase in resistivity of the grain boundaries,¹⁹ the resistivity was expected to decrease with increasing zirconia content. These two conflicting factors on the resistivity of grain boundaries resulted in less difference in the conductivity at 1 kHz when the zirconia content was between 30 and 60 vol%.

Oxygen diffusivities of mullite/zirconia composites with various zirconia contents show percolation behavior with respect to zirconia content,³² though percolation behavior of electrical conductivities was not observed for mullite/zirconia composites. This could be attributed to less difference in the conductivities between mullite and zirconia. The oxygen diffusivity of zirconia was larger than that of mullite by at least 8 orders of magnitude; however, the difference in electrical conductivities at 1 MHz between mullite and zirconia was only about 2 orders of magnitude. Hence, the electrical conductivities of the composites do not reveal the percolation behavior.

D. Microstructural viewpoint

Figure 7 shows that MZY05 exhibited elongated grains of mullite, while mullite grains in MZY30 and MZY80 were equiaxed. From the SEM micrograph of MZY05 [Fig. 7(a)], it was concluded that zirconia was located at the grain boundaries of mullite and was isolated by mullite grains. It was inferred that the conductivity was still dominated by mullite as mentioned in the previous section, although the grain conductivity in MZY05 was increased because of the addition of zirconia. Figure 7(b) reveals that some zirconia particles became interconnected in MZY30. The conductivity would be significantly affected by zirconia. Figure 7(c) showed that mullite grains were surrounded by zirconia grains in MZY80. The rapid path of interconnected zirconia for

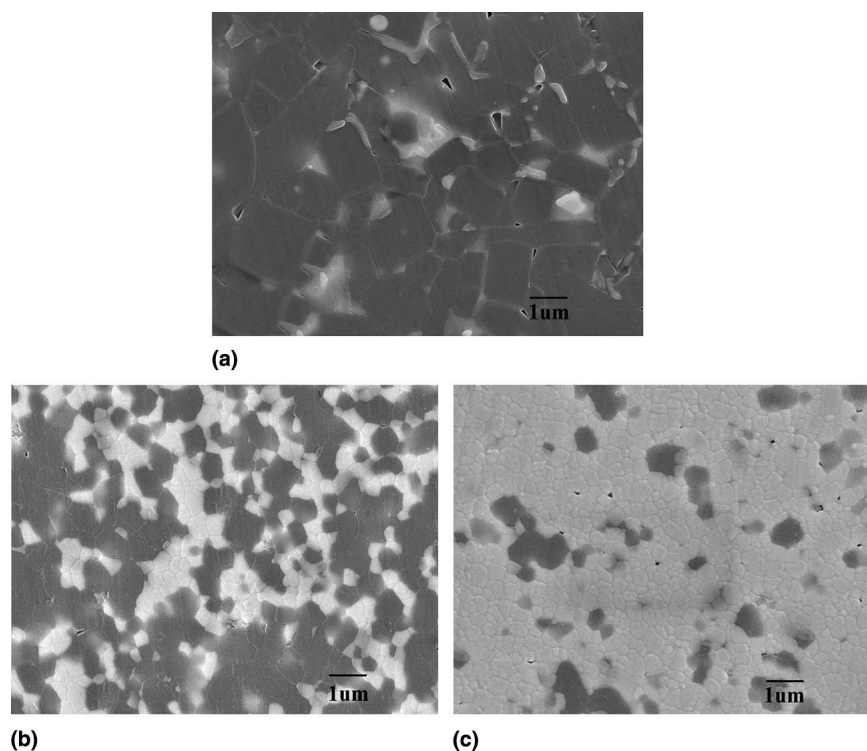


FIG. 7. Scanning electron micrographs of mullite/zirconia composites. (a) MZY05. (b) MZY30. (c) MZY80. The dark phase is mullite and the bright phase is zirconia.

electrical conductivity was formed in MZY80, and the grain and grain-boundary conductivities in MZY80 were completely controlled by zirconia.

IV. CONCLUSIONS

(1) The electrical conductivities of mullite/zirconia composites with various zirconia content were measured by the ac impedance spectroscopy. The impedance spectra of monolithic mullite showed only one semicircle, while the monolithic zirconia and mullite/zirconia composites showed two semicircles.

(2) The conductivities of mullite/zirconia composites increased with the zirconia content, but no percolation relationship was observed. The real parts of conductivities measured at 1 MHz and 1 kHz were in good agreement with the Lichtenecker's rule and the mixing rule, respectively.

(3) The activation energies of electrical conduction for mullite/zirconia composites were different in the high-frequency and low-frequency regions, depending on the zirconia content. The activation energies of grain conductivities in mullite and zirconia were about 65 and 79 kJ/mol, respectively, while those in the composites were calculated in between these two values. Furthermore, the activation energies sharply increased at 10 to 20 vol% ZrO_2 in the low-frequency region.

(4) The electrical conductivities of mullite/zirconia

composites were effectively increased by the incorporation of zirconia so that high-zirconia composites could be used for electrochemical purposes such as a gas sensor at high temperatures.

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