

Connectivity and Electrical Conductivity of YSZ-NiO Composite

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The electrical properties of the mixed conducting yttria (8 mol%) stabilized zirconia (YSZ)-nickel oxide (NiO) composites were examined by a.c. impedance, 4-probe d.c. conductivity between 400 and 1000°C. The oxygen partial pressure dependence of conductivity, and electromotive force measurement of galvanic cell enabled to determine the electronic contribution to the conduction. Up to 6 vol% NiO addition, the conductivity decreased since the electronic NiO acted as an insulator in ionic matrix. However the ionic transport was dominant until NiO content reaches 26 vol%. Mixed conduction was observed between 26 and 68 vol% of NiO. The effect of composition on the electrical property was explained by the microstructure and thus by the distribution of two phases.

Key words : Mixed conduction, YSZ, NiO, Composite

I. Introduction

Electrochemical devices based on solid electrolytes require the use of electrodes which conduct both ions and electrons for high efficiency and prolonged use.¹⁻⁴⁾ Materials that exhibit this property of conducting both ions and electrons are called mixed conductors.⁵⁾ Mixed conducting materials compatible with solid electrolyte are necessary for the successful operation of these electrochemical devices. Two different types of mixed conducting oxides may be classified. One is the single-phase material which shows both electronic and ionic conductivity in one material. The other is two-phase material composed of an electronic and an ionic conductor. YSZ containing aliovalent cation is an example of mixed conducting oxide in one phase.⁶⁻⁸⁾

Electrical composite materials are widely used in industrial applications such as resistors, sensors and transducers. Several types of electrical composites are possible which are composed of mixtures of ionic and electronic insulator or conductor. There has also been a considerable interest in the study of electrical properties of ionic-inert phase mixtures. Liang first studied the extraordinary increase in the ionic conductivity of LiI containing the inert insulator (Al_2O_3).⁹⁾ It has been reported that the dispersion of $\gamma\text{-Al}_2\text{O}_3$ in a matrix of halide electrolytes results in the increase of electrical conductivity by several orders of magnitude. The enhanced conduction could be attributed to the increased defect concentration due to space charge effects.^{10,11)} The electronic mixtures of nickel oxide-nickel sulfide and of nickel oxide and nickel or Pd also showed anomalous electrical conduction behavior.¹²⁻¹⁴⁾ The conductivity of the mixture of the p-type NiO and metallic conductor decreases initially,

attains minimum and increases with further addition of the metallic conductor. The result was explained by postulating the trapping of holes at the p-type-metallic conductor interface by the electrons from metallic conductor.

Sasaki *et al.* reported that the conductivity of ZrO_2 (ionic)- In_2O_3 (electronic) mixture decreases initially, attains minimum and increases with the further increase of In_2O_3 content.^{15,16)} The abrupt increase in the electrical conductivity with In_2O_3 concentrations higher than 45 mol% is caused by 3-dimensional connection of In_2O_3 phase. Wagner *et al.* reported the conductivity of CeO_2 -NiO mixture.¹⁷⁾ They explained that the initial decrease of electrical conductivity occurs by the trapping of transporting species at the CeO_2 -NiO interfaces.

Badwal *et al.* reported that the conductivity of 2.5 mol% Y_2O_3 doped ZrO_2 - Al_2O_3 mixture increases initially due to the grain boundary glassy phase, accumulating at the zirconia/alumina interfaces, attains maximum and decreases with the further increase of Al_2O_3 content at 400°C.¹⁸⁾ The conductivity of mixtures with 30 mol% Al_2O_3 was nearly the same as that of the sample with no Al_2O_3 .

YSZ-NiO is an example of ionic-electronic mixture. There are several advantages of choosing NiO as an electronic conductor and YSZ (8 mol% Y_2O_3 stabilized zirconia) as an ionic conductor. NiO and YSZ are stable at high temperature, their solubility in counterpart phase is limited, and the electrical conductivity of NiO is easily controlled by doping of acceptors such as Li_2O .¹⁹⁾ YSZ is an oxygen ion conductor and has many device applications such as sensors, fuel cells, oxygen pumps, electrochemical reactors and steam electrolysis cells. NiO is a typical metal deficient p-type semiconductor with cation vacancies and electron holes as primary defects. The undoped, stoichiometric NiO is an insulator but it is pos-

sible to increase the electrical conductivity of NiO by adding Li_2O .^{19,21)} YSZ-NiO mixtures having electron hole and oxygen ion at relatively high P_{O_2} are being studied as a potential cathode material for SOFC (solid oxide fuel cell) by adjusting the relative magnitude of ionic and electronic conductivity.

In this work, mixed conducting yttria (8 mol%) stabilized zirconia-nickel oxide composites were prepared in full composition range and the electrical conductivity of the composites was measured by a.c. impedance and 4-probe d.c. conductivity to determine the compositional dependence of conductivity and grain boundary contribution to total conductivity. EMF measurement of the galvanic cell and the oxygen partial-pressure dependent conductivity has also been used to determine the contribution of the ionic and electronic charge carriers on the conductivity. The distribution of two phases are studied as a function of composition.

II. Experimental Procedure

NiO (99.9%, High Purity Chemicals) and YSZ (8 mol% Y_2O_3 doped ZrO_2 , TZ8Y, TOSHO) powders were used to prepare YSZ-NiO composites with NiO content varying 0~100 mol%. The mixtures of TZ8Y and NiO were ball milled for 12 hours and dried in air at 80°C for a few hours. They were calcined at 800°C for 5 hours. Pellets were formed by die-pressing and then isostatically cold pressed into a disc at 200 MPa. The compacted disc was then sintered at 1600°C for 4 hours in air. The heating and cooling rate were maintained at 3°C/min. The color of the sintered specimens varies from light brown to dark green with increasing NiO concentration. The relative sintered density of mixtures were above 97% of theoretical density. However the density of pure NiO was about 91%.

The total electrical conductivity of the YSZ-NiO composites was measured using 4-probe d.c. technique. Specimens were cut into rectangular bars of $2.8 \times 2.5 \times 10 \text{ mm}^3$. Platinum paste (No. 6082, Engelhard, USA) was applied as electrodes.

4-probe d.c. electrical conductivity was measured using current source (model 220, Keithley, USA) and nanovoltmeter (model 181, Keithley, USA). The electrical conductivity measurement were performed at temperatures between 400 and 1000°C in air. At 1010°C partial pressure dependent conductivity was studied between 1 and 10^{-4} atm P_{O_2} . The oxygen partial pressure was controlled by flowing oxygen and argon mixture using mass flow controller and was measured using a zirconia oxygen sensor. The EMF cells were used to determine the oxygen ion transference numbers. They were calculated from the open-circuit voltages of EMF cells using YSZ-NiO composite pellets as electrolytes. The specimens (about 2 cm in diameter and 2 mm in thickness) were glass sealed to alumina tube. Air ($P_{\text{O}_2}=0.21$) flowed outside the alumina tube and oxygen ($P_{\text{O}_2}=1.0$) inside. Ionic transference

number(t_i) was defined by eq. [1].

$$\text{EMF} = t_i \frac{RT}{4F} \ln \frac{P_{\text{O}_2}(1.0)}{P_{\text{O}_2}(0.21)} \quad (1)$$

R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), T is the temperature(K) and F is the Faraday constant ($96,487 \text{ C/mol}$).

X-ray diffraction patterns with Cu- K_α radiation were obtained from the polished surface of the as-sintered samples using diffractometer (model D/MAX 3-C, Rigaku, Japan). The surface of the samples were thermally etched at 1450°C for 30 minutes and were examined under a scanning electron microscope (model 570, Hitachi, Japan) to determine the grain size.

III. Results and Discussion

In X-ray diffraction spectra of materials with nominal compositions $x\text{NiO}-(1-x)\text{YSZ}$, no other phase except NiO and YSZ was detected in all composition range. Small NiO peaks were detected from the samples with $x=0.1$. No NiO peaks were observed in samples with $x=0.02$ and 0.05. However, only 1% addition of YSZ in NiO resulted in the observation of YSZ peaks in NiO. The lattice parameter of stabilized zirconia decreases with increasing NiO concentration when the NiO concentration is less than about 2 mol%, indicating that the substitutional dissolution occurs with the replacement of Zr ion (tetravalent: 0.84 \AA) with Ni ion (tetravalent: 0.69 \AA).²²⁾ Above 2 mol% of NiO ($x=0.02$) addition, the lattice parameter of YSZ slightly decreases. The solubility limit of NiO in YSZ (8 mol% Y_2O_3 doped Zirconia) was also reported to be ~2 mol%.²³⁾

The grain size of YSZ slightly increases with increasing NiO concentration and reaches maximum value of 12 μm at 2 mol% ($x=0.02$). Above 2 mol% of NiO ($x=0.02$), the grain size continuously decreases. The grain size of NiO increases with 1 mol% YSZ addition and decreases above 1 mol% of YSZ ($x=0.99$). Assuming the concentration showing the maximum grain size as the solubility limit, i.e., for NiO in YSZ, the solubility limit is about ~2 mol% and for YSZ in NiO, it is ~1 mol%. Good matching was shown in the solubility limit of NiO in YSZ determined from the X-ray lattice parameter study and the grain size dependence.

Mole fractions are converted into volume fractions using 5.95 and 6.81 g/cm^3 as density values of YSZ and NiO, respectively. Samples were named according to their NiO vol% in the composite (hereafter $y\text{NYSZ}$, y is the vol% of NiO).

The ionic transference numbers shown in Fig. 1 confirmed the connection from one electrode to opposite electrode, i.e., the percolation by NiO phase near $y=40$. Until y reaches 26, the ionic conduction dominates. When y is between 26 and 68, the composites are mixed conducting by oxygen ions in YSZ and holes in NiO. When y increases above 60, the electron holes of NiO are main charge carriers. The percolation is also confirmed by the

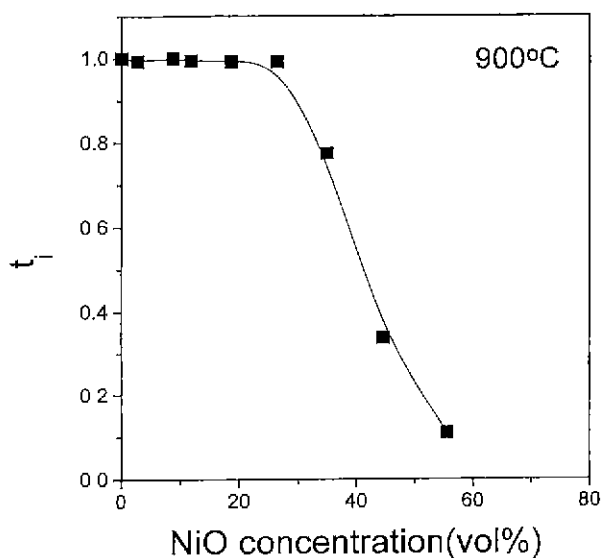


Fig. 1. Composition dependence of ionic transference number measured at 900°C.

effect of oxygen partial pressure on the electrical conductivity as shown in Fig. 2. Oxygen partial-pressure independent electrical conductivity is observed up to 26 vol% of NiO. But the slope increased to 1/4 at NiO content at or above 68 vol%. The 1/4 slope is generally observed for NiO when singly charged Ni vacancies are predominant defect.¹⁴⁾ The results of EMF and oxygen partial pressure dependence of conductivity coincide well and show the change of conduction mechanism from the ionic to the electronic.

A.c. impedance patterns of composites were analyzed and shown to be composed of two semicircles, each representing grain and grain boundary process. Fig. 3

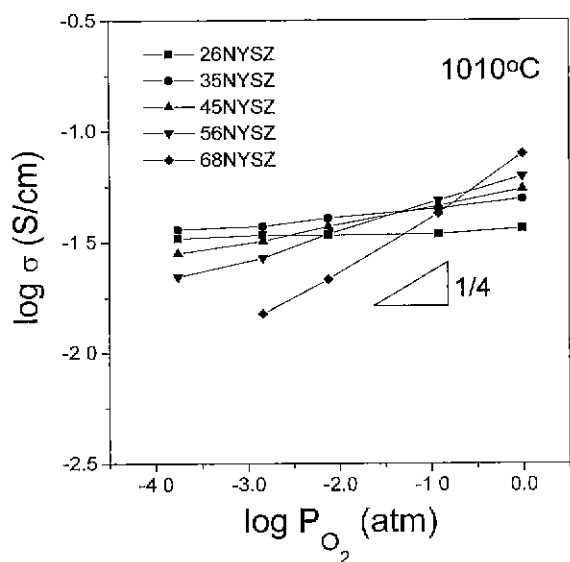


Fig. 2. Oxygen partial pressure dependence of electrical conductivities for composites with 26-68 vol% NiO addition at 1010°C.

shows the resistance ratio of grain to bulk (grain + grain boundary). In YSZ, the contribution of grain boundary to total resistivity is observed to be very small above 230°C. But with increasing NiO content, grain boundary resistance becomes dominant. With increasing temperature, the grain boundary resistance decreases and thus grain resistance is dominant in all composition range.

Fig. 4 shows grain conductivity of YSZ-NiO composites at 230°C. Up to 1.1 vol% of NiO, the electrical conductivity decreases due to the NiO dissolution in YSZ. In this region, additional oxygen vacancies generated by NiO addition in YSZ form vacancy-vacancy associates which lead to the reduction of the electrical conductivity.

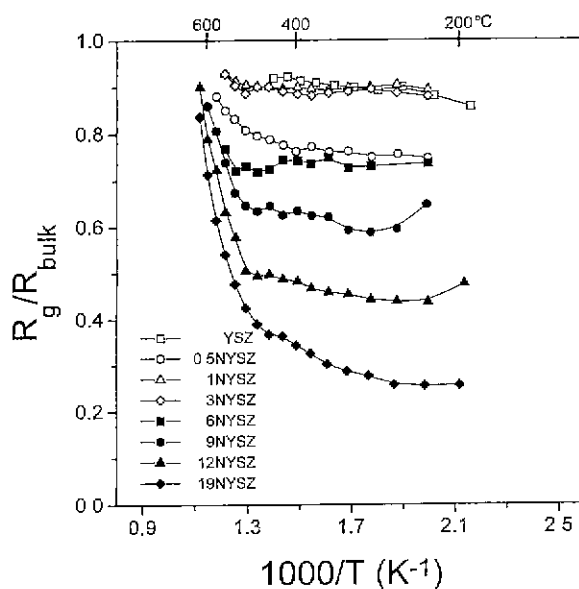


Fig. 3. Temperature and compositional dependence of resistance ratio of grain to bulk.

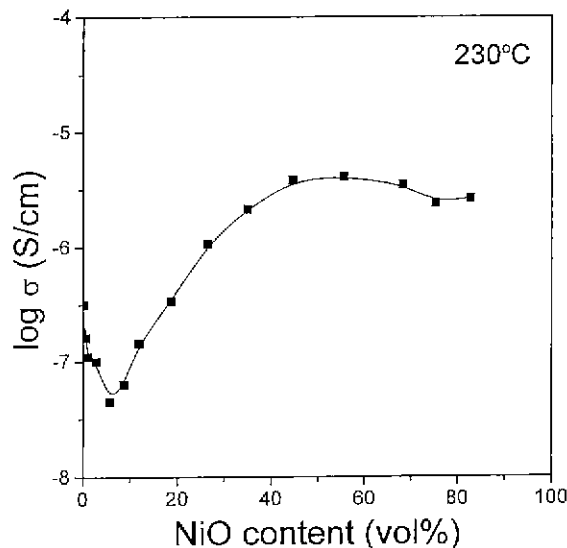


Fig. 4. Electrical conductivity of grain extracted from impedance data in YSZ-NiO composites measured at 230°C.

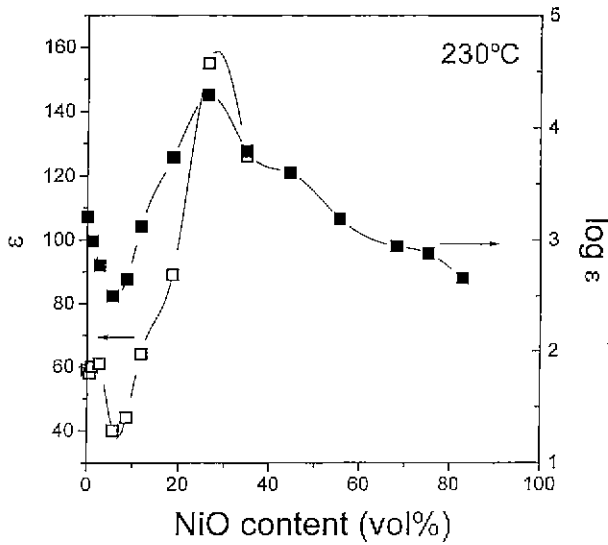


Fig. 5. Composition dependence of dielectric constant of grain (in linear scale) and the effective dielectric constant of grain boundary (in log scale) obtained from impedance data at 230°C.

Up to 6 vol% of NiO, the electrical conductivity decreases because discrete electronic NiO particles block the movement of ionic charge carriers in YSZ. When electronic NiO particles are discretely embedded in ionic YSZ matrix, their local electronic conductivity does not show up. In NiO, the oxygen conduction is very small, thus NiO blocks ionic charge carriers.

Fig. 5 shows the dielectric constant of grain (in linear scale) and the effective dielectric constant of grain boundary (in log scale). When NiO content is between 1 and 6 vol%, the dielectric constant of grain decreases due to discrete NiO particles which have lower dielectric constant ($\epsilon_r=6$) than YSZ particles ($\epsilon_r=60$). When NiO is between 6 and 26 vol%, NiO particles are partially connected each other and as a result, partially penetrating NiO particles reduce the shape factor of sample, thus the capacitance or the dielectric constant increases. When NiO content is above 26 vol%, the dielectric constant decreases again. In this composition range, NiO percolation is short-circuiting the ionic matrix and thus the capacitance decreases. The dielectric constant of grain boundary shows similar behavior.

Fig. 6 is the schematic diagram of the proposed two-dimensional microstructure of YSZ-NiO composites with composition. In this figure, the grain size of two phase was assumed to be same. When NiO content is less than 6 vol%, the NiO particles are discretely distributed and Fig. 6.a shows the distribution of black NiO particle in white YSZ matrix. Top and bottom of the samples are connected to the electrodes. When NiO content is between 6 and 26 vol%, the microstructure was schematically represented as that in Fig. 6.b In this composition range, NiO is connected to only one side of electrode and thus partially penetrating and discrete NiO particles coexist. Partially penetrating electronic NiO effectively

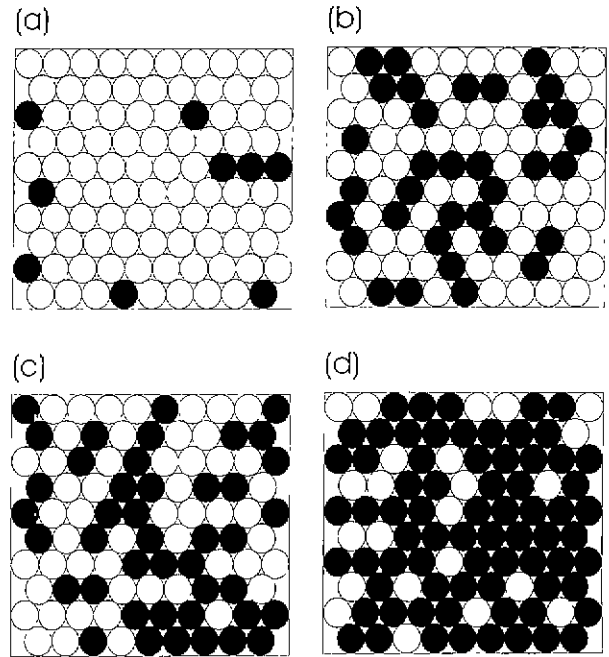


Fig. 6. Schematic diagram of the proposed 2-dimensional microstructure of YSZ-NiO composites with composition (yNiYSZ, y is vol% of NiO), (a) $y < 6$, (b) $6 < y < 26$, (c) $26 < y < 68$ and (d) $y > 68$. This is computer simulation of random distribution of two phases.²⁴⁾

reduces sample thickness and the length of oxygen ion conduction path thus increasing the electrical conductivity. When NiO content is between 26 and 68 vol%, percolation of NiO increases the electrical conductivity (Fig. 6.c). Fig. 6.d shows the distribution of discrete YSZ particles in NiO above 68 vol% of NiO.

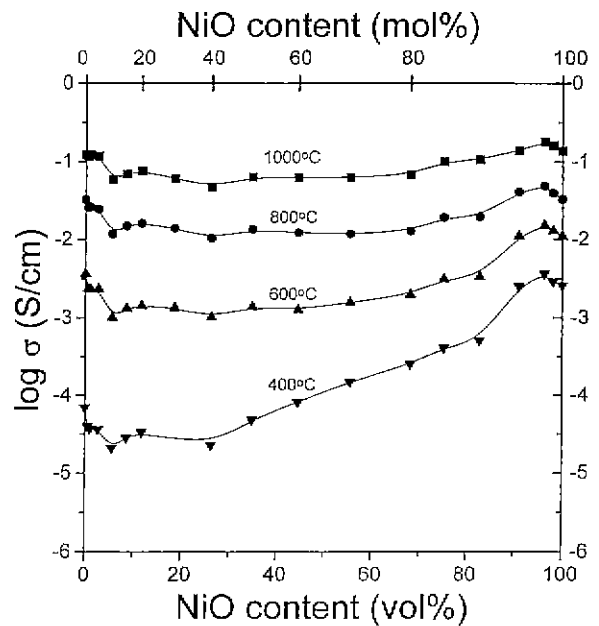


Fig. 7. Electrical conductivity of YSZ-NiO composites measured by 4-probe d.c. method.

Fig. 7 shows the electrical conductivity of YSZ-NiO composites obtained as a function of NiO concentration measured by four-probe method between 400 and 1000°C. The decrease of conductivity with NiO addition within the solubility limit is observed. Further drop of conductivity up to 6 vol% NiO addition is also clearly observed. When NiO content is between 26 and 68 vol%, the electrical conductivity of composites is shown to increase clearly with NiO content at 400°C. Above 400°C, conductivity was nearly the same in most of the compositions. However the relative contribution of electronic and ionic conduction changed with NiO content in this mixed conduction region. The percolation by NiO phase occurring at about 40 vol% observed with EMF measurement is not clearly observed in this figure. When NiO content is between 68 and 96 vol%, composites are electronic conductors with electron-holes of NiO as charge carriers and the electrical conductivity increases with NiO content.

IV. Conclusion

The electrical properties of YSZ-NiO mixtures were measured in the entire concentration range of the composite. The solubility of NiO in YSZ is about 2 mol%. Below 26 vol%(40 mol%) NiO content, the ionic conduction by YSZ prevails and above 68 vol%(80 mol%) NiO content, the electronic conduction by NiO prevails. The percolation and thus mixed conduction was observed for the samples with NiO content between 26 and 68 vol%.

For the composites with NiO content below 6 vol%, discrete NiO particles act as an insulator to YSZ and thus the electrical conductivity of composite decreases with increasing NiO. When NiO content is between 6 and 26 vol%, the partially penetrating NiO increases the electrical conductivity and capacitance. In mixed conduction region, NiO and YSZ were 3-dimensionally connected and the electrical conductivity increased with the addition of more conductive NiO content.

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