

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 July 2010 (08.07.2010)

(10) International Publication Number
WO 2010/077945 A2

(51) International Patent Classification:

H01M 8/12 (2006.01) *C01G 25/00* (2006.01)
C01F 7/02 (2006.01) *C01F 17/00* (2006.01)
C01G 45/02 (2006.01)

(21) International Application Number:

PCT/US2009/068253

(22) International Filing Date:

16 December 2009 (16.12.2009)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/201,977 17 December 2008 (17.12.2008) US

(71) Applicant (*for all designated States except US*): **SAINT-GOBAIN CERAMICS & PLASTICS, INC.** [US/US]; One Newbond Street, P.O. Box 15138, Worcester, MA 01615 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **NARENDAR, Yeshwanth** [US/US]; 34 Carlisle Road, Westford, MA 01886 (US). **LIN, Guangyong** [US/US]; 35 Westview Avenue, Shrewsbury, MA 01545 (US). **MOHANRAM, Aravind** [IN/US]; 45 Commons Drive, Apt. 34, Shrewsbury, MA 01545 (US).

(74) Agents: **PIERCE, N., Scott** et al.; Hamilton, Brook,smith & Reynolds, P.C., 5300 Virginia Road, P.O. Box 9133, Concord, MA 01742-9133 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report (Rule 48.2(g))*

(54) Title: CO-DOPED YSZ ELETROLYTES FOR SOLID OXIDE FUEL CELL STACKS

(57) Abstract: A solid oxide fuel cell electrolyte is fabricated by combining an yttria- stabilized zirconia powder with α - Al_2O_3 having a d_{50} particle size in a range of between about 10 nm and about 200 nm and Mn_2O_3 to form an electrolyte precursor composition, and then sintering the electrolyte precursor composition to thereby form the electrolyte. The α - Al_2O_3 and Mn_2O_3 can be present in the electrolyte precursor composition in an amount in a range of between about 0.25 mol% and about 5 mol%. The electrolyte can be a component of a solid oxide fuel cell of the invention.



WO 2010/077945 A2

-1-

CO-DOPED YSZ ELECTROLYTES FOR SOLID OXIDE FUEL CELL STACKS

RELATED APPLICATION

5 This application claims the benefit of U.S. Provisional Application No. 61/201,977, filed on December 17, 2008.

 The entire teachings of the above application are incorporated herein by reference.

BACKGROUND OF THE INVENTION

10 A fuel cell is a device that generates electricity by a chemical reaction. Among various fuel cells, solid oxide fuel cells use a hard, ceramic compound metal (*e.g.*, calcium or zirconium) oxide as an electrolyte. Typically, in solid oxide fuel cells, an oxygen gas, such as O₂, is reduced to oxygen ions (O²⁻) at the cathode, and a fuel gas, such as H₂ gas, is oxidized with the oxygen ions to form water at the
15 anode. Fuel cells are generally designed as stacks, whereby subassemblies, each including a cathode, an anode and a solid electrolyte between the cathode and the anode, are assembled in series by locating an electrical interconnect between the cathode of one subassembly and the anode of another.

 Zirconia stabilized by 8 mol% yttria (YSZ), such as, for example, from
20 Tosoh (Tosoh USA, Grove City, OH), or from Unitec Ceramics (Stafford, United Kingdom), or from Daiichi Kigenso Kagaku Kogyo (Osaka, Japan) is commonly used as the electrolyte of solid oxide fuel cells (SOFCs) as it has a high oxygen ion conductivity and is quite stable in both oxidant and fuel atmospheres. A preferred YSZ is TZ-8Y powder from Tosoh USA. However, its high sintering temperature
25 (about 1377 °C for TZ-8Y) limits its application in some areas such as co-firing multiple layers in the cell level and/or multiple cells in the stack level.

 Therefore, a new approach is needed to minimize or eliminate the above mentioned problems.

SUMMARY OF THE INVENTION

This invention generally is directed to a method of reducing the sintering temperature and modifying the sintering behavior of a YSZ electrolyte by co-doping α -Al₂O₃ having a d₅₀ particle size in a range of between about 10 nm and about 200 nm, and Mn₂O₃ (each independently in a range of between about 0.25 mol% and about 5 mol%) so as to improve the performance of SOFCs and reduce the cost of the SOFC stack manufacture.

In one embodiment, the invention is directed to a method for forming an electrolyte of a solid oxide fuel cell that includes the steps of combining an yttria-stabilized zirconia powder with α -Al₂O₃ and Mn₂O₃ to form an electrolyte precursor composition, and sintering the electrolyte precursor composition to thereby form the electrolyte. The α -Al₂O₃ and Mn₂O₃ can be present in the electrolyte precursor composition in an amount in a range of between about 0.25 mol% and about 5 mol%. In a specific embodiment, the α -Al₂O₃ and Mn₂O₃ is present in the electrolyte precursor in an amount of about 2 mol%. In some embodiments, the composition of the yttria-stabilized zirconia powder includes at least one of: yttria in an amount between about 3% and about 10 mol% of the powder; and zirconia in an amount in a range of between about 90 mol% and about 97 mol% of the powder. In a specific embodiment, yttria is present in the yttria-stabilized zirconia powder in an amount of about 8 mol%.

In some embodiments, the d₅₀ particle size of the yttria-stabilized zirconia powder is in a range of between about 0.05 μ m and about 1 μ m. The ratio of α -Al₂O₃:Mn₂O₃ can be in a range of between about 0.25:1 and about 1:0.25. The d₅₀ of the α -Al₂O₃ can be in a range of between about 10 nm and about 200 nm. In a specific embodiment, the d₅₀ of the α -Al₂O₃ is about 50 nm. The specific surface area of α -Al₂O₃ can be in a range of between about 5 m²/g and about 30 m²/g. In a specific embodiment, the specific surface area of the α -Al₂O₃ is about 17 m²/g. The d₅₀ of the Mn₂O₃ can be in a range of between about 50 nm and about 400 nm. In a specific embodiment, the d₅₀ of the Mn₂O₃ is about 200 nm. The specific surface area of the Mn₂O₃ can be in a range of between about 10 m²/g and about 50 m²/g. In a specific embodiment, the specific surface area of Mn₂O₃ is about 32 m²/g. The d₅₀ of the yttria-stabilized zirconia (YSZ) powder can be in a range of between about 50

nm and about 1000 nm. In a specific embodiment, the d_{50} of the YSZ is about 250 nm. The specific surface area of the YSZ can be in a range of between about 5 m²/g and about 30 m²/g. In a specific embodiment, the specific surface area of the YSZ is about 13 m²/g.

- 5 In another embodiment, the invention is directed to an electrolyte of a solid oxide fuel cell that is doped with α -Al₂O₃ and Mn₂O₃. In yet another embodiment, the invention is directed to a solid oxide fuel cell that includes an electrolyte component doped with α -Al₂O₃ and Mn₂O₃.

- This invention has many advantages, including a reduction in the peak
10 temperature (T_{max}) from about 1377°C for pure YSZ to about 1226 °C for 2.0 mol% α -Al₂O₃ + Mn₂O₃. Furthermore, dilatometry dL/dT full width half maximum (FWHM) was increased from about 181 °C for pure YSZ to about 281 °C for 2.0 mol% α -Al₂O₃ + Mn₂O₃. In addition, co-doping α -Al₂O₃+ Mn₂O₃ showed improved relative density (up to 6% improvement) with the same hot pressing procedure
15 compared to α -Al₂O₃-doping and Mn₂O₃-doping. These properties enable the production of improved SOFC stacks.

BRIEF DESCRIPTION OF THE DRAWINGS

- The foregoing will be apparent from the following more particular description of example embodiments of the invention, as illustrated in the
20 accompanying drawings. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating embodiments of the present invention.

FIG. 1 is an SEM photograph showing the particle size of Tosoh TY-8Y powder.

- FIG. 2 is an SEM photograph showing the particle size of ultrafine α -Al₂O₃
25 (provided by Saint-Gobain (SG) Greens and Powders Group).

FIGS. 3A-B are SEM photographs showing the particle sizes of (A) as-received Mn₂O₃ and (B) after attrition milling for 42 hrs.

- FIGS. 4A-B are graphs of the median particle diameter (d_{50}) of Mn₂O₃ after attrition milling measured with laser light scattering. (A) The median diameter (d_{50})
30 of Mn₂O₃ after attrition milling with changing milling media from d=2.0mm for 4 hrs to d=0.3mm for 38 hrs. (B) The median diameter (d_{50}) of Mn₂O₃ after attrition milling using milling media of d=2.0mm for 30 hrs.

FIG. 5 is a graph of the shrinkage rate of TZ-8Y doped with SG ultrafine- α - Al_2O_3 as measured by dilatometry using water at a pH value of 3 (acidified with nitric acid) for mixing with binders.

FIG. 6 is a graph of the shrinkage rate of TZ-8Y doped with SG ultrafine- α - Al_2O_3 as measured by dilatometry using ethanol for mixing without binders.

FIG. 7 is a graph of the shrinkage rate of YSZ doped with ultrafine- α - Al_2O_3 as measured by dilatometry using water for mixing with binders.

FIG. 8 is a graph of the shrinkage rate of YSZ doped with Mn_2O_3 as measured by dilatometry using water for mixing with binders.

FIGS. 9A-B are graphs of the shrinkage rate of YSZ doped with ultrafine- α - Al_2O_3 and Mn_2O_3 as measured by dilatometry using water for mixing with binders. (A) 50%/50% of α - Al_2O_3 / Mn_2O_3 and (B) at fixed 0.5 mol% α - Al_2O_3 and various Mn_2O_3 amounts.

FIG. 10 is a graph of the measured densities of undoped YSZ and doped YSZ after pressurelessly sintering at 1380 °C for 1 hr.

FIG. 11 is a graph of the relative density of ultrafine- α - Al_2O_3 doped YSZ measured during hot pressing T1P2 cycle.

FIG. 12 is a graph of the relative density of Mn_2O_3 doped YSZ measured during hot pressing T1P2 cycle.

FIG. 13 is a graph of the relative density of α - Al_2O_3 + Mn_2O_3 (equi-molar) co-doped YSZ measured during hot pressing T1P2 cycle.

FIG. 14 is a graph of the relative density of doped YSZ (with equi-molar α - Al_2O_3 + Mn_2O_3) measured during hot pressing under T1(1380 °C), P2 (low pressure) and T1(1380 °C), XP13 (high pressure).

FIG. 15 is a graph of the relative density of doped YSZ (with equi-molar α - Al_2O_3 + Mn_2O_3) measured during hot pressing XT5 (1320 °C), XP7 and XT5 (1320 °C), XP12.

FIGS. 16A-E are SEM photographs of undoped and doped YSZs (with equi-molar α - Al_2O_3 + Mn_2O_3) after T1, P2 profiles hot pressing: (A) undoped YSZ, (B) E0616, (C) 1.5 mol% Mn_2O_3 doped YSZ, (D) 0.25mol% α - Al_2O_3 +0.25mol% Mn_2O_3 doped YSZ, and (E) 0.75mol% α - Al_2O_3 +0.75mol% Mn_2O_3 doped YSZ.

FIGS. 17A-D are SEM photographs of doped YSZs (with equi-molar α - Al_2O_3 + Mn_2O_3) after XT5, XP7 profiles hot pressing: (A) E0616, (B) 0.25mol%

$\text{Al}_2\text{O}_3 + 0.25\text{mol}\%$ Mn_2O_3 doped YSZ, (C) $0.75\text{mol}\%$ $\text{Al}_2\text{O}_3 + 0.75\text{mol}\%$ Mn_2O_3 doped YSZ, and (D) $1.5\text{mol}\%$ Mn_2O_3 doped YSZ.

FIGS. 18A-D are SEM photographs of undoped and doped YSZ samples after pressurelessly sintered at 1380°C for 1hr: (A) Undoped YSZ, (B) $0.5\text{mol}\%$ $\alpha\text{-Al}_2\text{O}_3$ doped YSZ, (C) $2.0\text{mol}\%$ $\alpha\text{-Al}_2\text{O}_3$ doped YSZ and (D) $2.0\text{mol}\%$ Mn_2O_3 doped YSZ.

FIG. 19 is a graph of the open circuit voltages (OCV) of symmetrical cells using undoped and doped YSZ (with equi-molar $\alpha\text{-Al}_2\text{O}_3 + \text{Mn}_2\text{O}_3$) as the electrolytes with humidified H_2 ($3\%\text{H}_2\text{O}$) as the fuel and air as the oxidant.

10 DETAILED DESCRIPTION OF THE INVENTION

A description of example embodiments of the invention follows.

Zirconia stabilized by $8\text{mol}\%$ yttria (YSZ), such as, for example, from Tosoh (Tosoh USA, Grove City, OH), or from Unitec Ceramics (Stafford, United Kingdom), or from Daiichi Kigenso Kagaku Kogyo (Osaka, Japan) is commonly used as the electrolyte of solid oxide fuel cells (SOFCs) as it has a high oxygen ion conductivity and is quite stable in both oxidant and fuel atmospheres. A preferred YSZ is TZ-8Y powder from Tosoh USA. However, its high sintering temperature (about 1377°C for TZ-8Y) limits its application in some areas such as co-firing multiple layers in the cell level and/or multiple cells in the stack level.

The invention generally is directed to a method of reducing the sintering temperature and modifying the sintering behavior of the YSZ electrolyte by doping ultrafine- $\alpha\text{-Al}_2\text{O}_3$, having a d_{50} particle size in a range of between about 10nm and about 200nm , and Mn_2O_3 , and/or co-doping $\alpha\text{-Al}_2\text{O}_3 + \text{Mn}_2\text{O}_3$ so as to improve the performance of SOFCs and reduce the cost of the SOFC stack manufacture.

Doping $\alpha\text{-Al}_2\text{O}_3$, Mn_2O_3 , and Co_3O_4 into YSZ can significantly improve the sintering behavior by reducing the sintering temperature. NiO also reduces the sintering temperature of YSZ, but not as much as Mn_2O_3 . Y. Ji, J. Liu, Z. Lu, X. Zhao, T. He, and W. Su, *Study on the properties of Al_2O_3 -doped $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ electrolyte*, Solid State Ionics 126(1999) 277-283. It is known that there is a compensating effect of co-doping Mn_2O_3 and Co_3O_4 in both sintering and electrical properties. It has been shown that Mn decreases the electronic conductivity of YSZ, while Co increases it. Cells with Co_3O_4 doped and/or Mn_2O_3 and Co_3O_4 co-doped

YSZ as the electrolytes show very low open circuit voltages (OCV), and therefore Co_3O_4 is not a preferred dopant. Co-doping $\alpha\text{-Al}_2\text{O}_3$ and Mn_2O_3 reduces the sintering temperature and improves the sintering behavior of the YSZ electrolyte more than does single-doping $\alpha\text{-Al}_2\text{O}_3$ and Mn_2O_3 .

5 The sintering temperature and densification behavior of 8 mol% yttria stabilized zirconia (YSZ) can be significantly reduced and modified by adding one or two ultrafine cation dopants in a conventional ceramic process. A small amount (in a range of between about 0.25 mol% and about 5 mol%) of ultrafine (having a d_{50} particle size in a range between about 10 nm and about 200 nm, preferably about
10 50 nm median particle diameter) $\alpha\text{-Al}_2\text{O}_3$, Mn_2O_3 doping, and $\alpha\text{-Al}_2\text{O}_3 + \text{Mn}_2\text{O}_3$ co-doping can significantly reduce the peak temperature of the shrinkage (dL/dT) curve (over 200 °C with 0.5mol% $\alpha\text{-Al}_2\text{O}_3$ +1.5mol% Mn_2O_3 co-doping) and the maximum shrinkage rate of YSZ. However, the dopants typically do not significantly increase the electronic conductivity of YSZ, such as, for example, Tosoh TZ-8Y. Therefore,
15 the open circuit voltage of cells using the doped YSZ as the electrolytes generally will be as good as using undoped YSZ. It becomes possible to densify the YSZ electrolyte at 1150~1200 °C with $\alpha\text{-Al}_2\text{O}_3$ + Mn_2O_3 co-doping.

 Sintering temperature is significantly reduced and sintering behavior of the YSZ electrolyte is modified by co-doping a small amount of ultrafine- $\alpha\text{-Al}_2\text{O}_3 +$
20 Mn_2O_3 so as to improve the performance of SOFC's and reduce the cost of the SOFC stack manufacture.

Exemplification

 Three powders, Tosoh TZ-8Y (YSZ) (Tosoh USA, Grove City, OH), ultrafine $\alpha\text{-Al}_2\text{O}_3$ from Greens and Powders (G&P) group of Saint-Gobain High
25 Performance Materials, and Mn_2O_3 from Alfa Aesar (Ward Hill, MA) were selected as the starting materials in this study. SEM and laser light scattering were used to characterize the as-received materials and those after attrition milling. The particle sizes were obtained by laser scattering measurements with a Partica LA-950 laser from Horiba (Horiba Instruments, Inc., Irvine, CA). The compositions of the
30 powder mixtures that were prepared are shown in Table 1. Deionized (DI) water with a pH value of 3 (acidified with nitric acid), ethanol, and DI water with 3 wt% of Darvan C (R. T. Vanderbilt, Inc., Norwalk, CT) as the dispersant plus 3 minutes

ultrasonic treatment were three techniques used to optimize dispersing ultrafine α - Al_2O_3 in YSZ. Then, the optimized technique were used to mix Mn_2O_3 doped YSZ and α - Al_2O_3 + Mn_2O_3 co-doped YSZ powders. The sintering behaviors of the three doped YSZ series were studied by pressureless sintering, dilatometry, and hot pressing. Densities of doped YSZ samples were measured for the free sintering samples by the Archimedes method that is well known in the art, and image analysis (IA) processing by SEM and /or dimension shrinkage calculation by a laser for the hot pressed samples.

Also, the total and electronic conductivities of selected compositions of the three doped YSZ series were measured by a two-probe technique. The open circuit voltages (OCV) of symmetric cells using undoped YSZ and some doped YSZs as the electrolytes were measured at 800, 900, and 1,000 °C with Pt paste as the electrodes, humidified hydrogen as the fuel and air as the oxidant.

Results and Discussion

Materials Characterizations

The SEM and laser scattering results (as shown in Figures 1 to 3) showed that the YSZ powder had a specific surface area (SSA) of $12.99 \text{ m}^2/\text{g}$ and a median particle size (d_{50}) of $0.25 \mu\text{m}$ (Figure 1); ultrafine- α - Al_2O_3 powder had an SSA of $16.8 \text{ m}^2/\text{g}$ and a d_{50} of 50nm (data and picture were provided by G&P as shown in Figure 2); Mn_2O_3 powder had an SSA of $1.04 \text{ m}^2/\text{g}$ and a d_{50} of $3.98\mu\text{m}$ (Figure 3(a)). The as-received ultrafine- α - Al_2O_3 powder was ready to dope YSZ powder while the as-received Mn_2O_3 powder was refined further by attrition milling. The as-received Mn_2O_3 powder was attrition-milled at a ratio of 10:1:2 for media: solid: vehicle (DI water) and a speed of 500 rpm to reduce the particle size. Samples were collected after different milling periods to measure the particle size distribution by laser light scattering using a Partica LA-950 from Horiba Co. (Horiba Instruments, Inc., Irvine, CA). Figure 4(a) showed that the median particle size (d_{50}) of Mn_2O_3 could be reduced from as-received $4.0 \mu\text{m}$ to $0.2 \mu\text{m}$ after 24 hours attrition milling, but it was not reduced more by 18 more hours milling with the same condition. The specific surface area (SSA) of Mn_2O_3 was increased from $1.04 \text{ m}^2/\text{g}$ to $31.59 \text{ m}^2/\text{g}$ after attrition milling. The ZrO_2 milling media was changed from $d=2.0\text{mm}$ after 4

hrs milling to $d=0.3\mu\text{m}$ during the rest of attrition milling. Alternatively, a d_{50} of $0.32\mu\text{m}$ and an SSA of $26.19\text{ m}^2/\text{g}$ of Mn_2O_3 could be obtained after 30 hrs attrition milling using the ZrO_2 milling media of $d=2.0\text{mm}$, as shown in Figure 4(b). The Mn_2O_3 powder with a d_{50} of $0.2\mu\text{m}$ and an SSA of $31.59\text{ m}^2/\text{g}$ was used to dope

5 YSZ for the sintering study, although it was larger than the expected particle size (a d_{50} of $0.1\mu\text{m}$). Figure 3(b) showed the particle size of Mn_2O_3 after attrition milling for 42 hours.

Table 1. Compositions of YSZ powders doped with ultrafine- α -Al₂O₃ and Mn₂O₃

Sample No.	Dopant	Dopant mol.%	Dopant wt.%	YSZ wt.%
0		0	0	100 wt.%
0.2	α -Al ₂ O ₃	0.2	0.1557	99.8443
1	α -Al ₂ O ₃	0.5	0.3883	99.6117
2	α -Al ₂ O ₃	1	0.7775	99.2225
3	α -Al ₂ O ₃	1.5	1.1676	98.8324
4	α -Al ₂ O ₃	2	1.5586	98.4414
5	Mn ₂ O ₃	0.25	0.3002	99.6998
6	Mn ₂ O ₃	0.5	0.6000	99.4000
7	Mn ₂ O ₃	1	1.1989	98.8011
8	Mn ₂ O ₃	1.5	1.7965	98.2035
9	Mn ₂ O ₃	2	2.3929	97.6071
Co-doped 50%/50% of				
10	α -Al ₂ O ₃	0.25	0.1940	99.5057
	Mn ₂ O ₃	0.25	0.3003	
11	α -Al ₂ O ₃	0.5	0.3879	99.0114
	Mn ₂ O ₃	0.5	0.6007	
12	α -Al ₂ O ₃	0.75	0.5819	98.5170
	Mn ₂ O ₃	0.75	0.9011	
13	α -Al ₂ O ₃	1	0.7760	98.0225
	Mn ₂ O ₃	1	1.2015	
14	α -Al ₂ O ₃	0.5	0.3875	98.4123
	Mn ₂ O ₃	1.0	1.2002	
15	α -Al ₂ O ₃	0.5	0.3872	97.8144
	Mn ₂ O ₃	1.5	1.7985	

3.2. Optimizing the technique for mixing ultrafine Al_2O_3 and YSZ powder

DI water with a pH value of 3 (acidified with nitric acid), ethanol, and DI water with 3 wt% of Darvan[®] C as the dispersant plus 3 minutes ultrasonic treatment were respectively used to optimize the technique for dispersing ultrafine- Al_2O_3 .

- 5 Figure 5 shows the first derivative of the shrinkage curves as measured by dilatometry for powder mixtures prepared with 0.0, 0.5, 1.0, 1.5, 2.0 mol% $\alpha\text{-Al}_2\text{O}_3$ added to YSZ using DI water at a pH value of 3 (acidified with nitric acid) for mixing. $\alpha\text{-Al}_2\text{O}_3$ and YSZ powders were added into the DI water at the same time and ball milled for 24 hrs, followed by addition of binders which were used to
- 10 improve die-pressing, which were added one hour before the end of ball milling. A similar result has been achieved when using a d_{50} of 0.3 μm Al_2O_3 as the dopant. The onset of sintering was basically unchanged by $\alpha\text{-Al}_2\text{O}_3$ doping, but the increase in the shrinkage rate with temperature occurred much faster, compared to the undoped YSZ. As a result, the peak temperature of the (dL/dT) curve was reduced
- 15 by 100 $^\circ\text{C}$, compared to 80 $^\circ\text{C}$ when using a d_{50} of 0.3 μm $\alpha\text{-Al}_2\text{O}_3$. The peak sintering temperature was almost unchanged over the four dopant levels tested. This is most likely due to the low solubility limit of $\alpha\text{-Al}_2\text{O}_3$ in YSZ. The magnitude of the $(dL/dT)_{\text{max}}$ showed an inverse relationship with $\alpha\text{-Al}_2\text{O}_3$ dopant level and is lower than the $(dL/dT)_{\text{max}}$ obtained using a d_{50} of 0.3 μm $\alpha\text{-Al}_2\text{O}_3$. As shown in
- 20 FIGS. 5 and 6, the (dL/dT) curves became broader when using ultrafine- $\alpha\text{-Al}_2\text{O}_3$ doping. Figure 6 shows the (dL/dT) curves of ultrafine- $\alpha\text{-Al}_2\text{O}_3$ doped YSZ powder mixtures of the same composition as shown in Figure 5 but using ethanol for mixing (ball milling for 24 hrs) without adding binders. The two figures demonstrated similar sintering behaviors for the $\alpha\text{-Al}_2\text{O}_3$ doped YSZ powders using either DI
- 25 water with a pH value of 3 (acidified with nitric acid) or ethanol for mixing although the $(dL/dT)_{\text{max}}$ in Figure 6 is slightly higher than that in Figure 5 for each composition. However, neither DI water with a pH value of 3 (acidified with nitric acid) nor ethanol is acceptable for SOFC tape casting technology if water-based tape casting technology is used and the binders system will not work in the acid
- 30 environment (at the pH value of 3) so that in a preferred mixing technique only DI water with 3 wt% Darvan[®] C as the dispersant was used to mix the ultrafine- $\alpha\text{-Al}_2\text{O}_3$ powder and YSZ powder and an ultrasonic probe with a power of 60 watts

was used to disperse the ultrafine α -Al₂O₃ powder in the DI water for 3 minutes, then the dopant was ball milled first for 4 hrs before adding YSZ powder. Binders for improving die-pressing were also added one hour before the end of ball milling. The total ball milling time was 24 hrs. SEM result showed that ultrafine α -Al₂O₃ particles were dispersed more homogeneously and hardly agglomerated in the YSZ matrix. The preferred mixing method described above also improved the relative density of 2 mol% α -Al₂O₃ doped YSZ by about 2% when pressurelessly sintered at 1380 °C for 1 hr, that is, the doped YSZ reached 97.5% relative density compared to 95.5% when mixed using DI water at a pH value of 3 (acidified with nitric acid) and sintered together at 1380 °C for 1 hr. Based on the results of the above trials, the powder mixtures with compositions as shown in Table 1 were prepared using the preferred mixing method and submitted to additional processing. Three bar samples of 4mmx4mmx25mm for each composition were pressurelessly sintered at 1380 °C for 1 hr for density measurement by the Archimedes method.

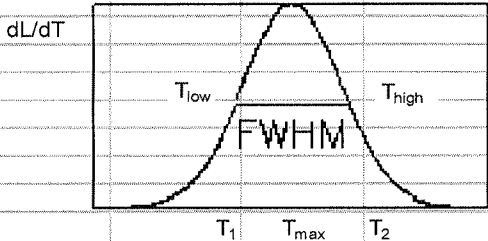
Sintering behaviors of undoped YSZ and doped YSZ in dilatometry and densities by free sintering

The sintering behaviors of three doped YSZ series were studied by dilatometry and free sintering. Figures 7 to 9 show the first derivative of the shrinkage curves as measured by dilatometry for ultrafine- α -Al₂O₃, Mn₂O₃, and Al₂O₃+Mn₂O₃ doped YSZ powder mixtures, respectively (their compositions are listed in Table 1). Some important parameters from the dL/dT curves are defined and summarized in Table 2. All the powder mixtures were prepared using the same procedure described below, which is favorable to the water-based SOFC tape casting technology, because the binders used in the water-based SOFC tape casting technology will not be dissolved in ethanol and will be decomposed in the acid environment (at the pH value of 3), and favorable to ensure that dopants are distributed homogeneously in the YSZ matrix as shown above. DI water with 3 wt% Darvan[®] C as the dispersant was used to mix the dopant powders and YSZ powder and an ultrasonic probe with a power of 60 watts was used to disperse the dopant powders in the DI water for 3 minutes, then the dopants were ball milled first

for 4 hrs before adding YSZ powder. Binders for improving die-pressing were also added one hour before the end of ball milling. The total ball milling time was 24 hrs.

As shown in Figures 7 to 9 as well as in Table 2, over all, the $(dL/dT)_{\max}$ and the peak temperature (T_{peak}) of the (dL/dT) curve were reduced with dopants. The $(dL/dT)_{\max}$ was reduced from 0.1075 for pure YSZ to 0.0825 with 2.0 mol% Al_2O_3 , to 0.0811 with 2.0 mol% Mn_2O_3 , and to 0.0757 with 2.0 mol% $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$. The peak temperature (T_{peak}) was reduced from 1377 °C for pure YSZ to 1268 °C with 0.5 mol% Al_2O_3 , to 1205 °C with 2.0 mol% Mn_2O_3 , to 1226 °C with 1.0 mol% $\text{Al}_2\text{O}_3+1.0$ mol% Mn_2O_3 , and to 1170 °C with 0.5 mol% $\text{Al}_2\text{O}_3+1.5$ mol% Mn_2O_3 . The T_{peak} of Al_2O_3 doped YSZ recovered slightly with higher dopant levels, to 1288 °C with 2.0 mol% Al_2O_3 . All the (dL/dT) curves became broader with dopants. The full width half maximum (FWHM) could be increased from 181 °C for pure YSZ to 281 °C with 2.0 mol% $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$. The asymmetry, γ , of the (dL/dT) curves, in most cases, was reduced with dopants, except for 0.25 and especially for 0.5 mol% Mn_2O_3 doping, as shown in FIG. 8. It can be concluded that $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$ co-doping has more significant effects on the sintering behaviors of YSZ than separate Al_2O_3 doping and Mn_2O_3 doping, that is, $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$ co-doping improves YSZ densification more than only Al_2O_3 doping or only Mn_2O_3 doping.

Table 2. Summary of dilatometry results for Al₂O₃, Mn₂O₃, and Al₂O₃+Mn₂O₃ doped YSZ

Al ₂ O ₃ doped YSZ						
Dopant(mol%)	(dL/dT)max	T _{peak}	T ₁	T ₂	FWHM	γ
0	0.1075	1377	1255	1436	181	2.0678
0.2	0.1077	1285	1186	1380	194	1.0421
0.5	0.0951	1268	1165	1387	222	0.8655
1	0.0917	1273	1153	1392	239	1.0084
1.5	0.0826	1288	1150	1402	252	1.2105
2	0.0825	1288	1152	1403	251	1.1826
Mn ₂ O ₃ doped YSZ						
Dopant(mol%)	(dL/dT)max	T _{peak}	T ₁	T ₂	FWHM	γ
0	0.1075	1377	1255	1436	181	2.0678
0.25	0.092	1357	1206	1423	217	2.2879
0.5	0.0853	1326	1168	1374	206	3.2917
1	0.0802	1282	1120	1382	262	1.6200
1.5	0.0775	1255	1084	1351	267	1.7813
2	0.0811	1205	1067	1325	258	1.1500
Al+Mn doped YSZ with 50/50mol% of Al ₂ O ₃ /Mn ₂ O ₃						
Dopant(mol%)	(dL/dT)max	T _{peak}	T ₁	T ₂	FWHM	γ
0	0.1075	1377	1255	1436	181	2.0678
0.5	0.0935	1301	1158	1378	220	1.8571
1	0.0814	1251	1112	1371	259	1.1583
1.5	0.0805	1255	1089	1361	272	1.5660
2	0.0757	1226	1068	1349	281	1.2846
Al+Mn doped YSZ with fixed 0.5 mol% Al ₂ O ₃						
Dopant(mol%)	(dL/dT)max	T _{peak}	T ₁	T ₂	FWHM	γ
0	0.1075	1377	1255	1436	181	2.0678
0.5Al+0Mn	0.0951	1268	1165	1387	222	0.8655
0.5Al+0.5Mn	0.0814	1251	1112	1371	259	1.1583
0.5Al+1.0Mn	0.0973	1228	1082	1308	226	1.8250
0.5Al+1.5Mn	0.0942	1170	1060	1289	229	0.9244
FWHM=Full-Width Half-Maximum						
Asymmetry:						
$\gamma = (T_{max}-T_{low})/(T_{high}-T_{max}) = (T_{max}-T_1)/(T_2-T_{max})$						
						

The measured densities and relative densities of Al₂O₃ doped YSZ, Mn₂O₃ doped YSZ, and Al₂O₃+Mn₂O₃ (equi-molar) co-doped YSZ bar samples (all three series) after die-pressing and then pressurelessly sintering at 1380 °C for 1 hr are shown in Figure 10. The densities were measured by the Archimedes method. The theoretical densities of the doped YSZs used to calculate the relative densities were

calculated by using the mixture rule of composites and the theoretical densities of YSZ, Al_2O_3 and Mn_2O_3 , assuming no solubility or reaction between these components. As shown in Figure 10, none of doping with Al_2O_3 , Mn_2O_3 , and $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$ had a significant effect on improving the densification of Tosoh TZ-8Y at this temperature probably because YSZ powder, such as, for example, Tosoh TZ-8Y, usually has good sinterability at such a high temperature when pressurelessly sintering. The sintering temperature of about 1380 °C was selected because it was the preferred temperature for hot pressing SOFCs. However, the chosen sintering temperature was substantially higher than the T_{peak} of doped YSZ, as shown in Table 2, so that all the doped YSZs could be oversintered at 1380 °C, which would reduce the densities. Another reason that Al_2O_3 doped YSZ had a slightly lower density could be that the best mixing technique for dispersing ultrafine Al_2O_3 in YSZ developed here was still not perfect. Usually, agglomeration will cause low densification.

Sintering behaviors of undoped YSZ and doped YSZ in hot pressing

The sintering behaviors of selected materials were studied by hot pressing. Preliminary results are shown in Figures 11 to 13. The materials selected for this study are Samples #0, #1, #3, #6, #8, #10 and #12. Their compositions are listed in Table 1. The data from a reference electrolyte E0616 (1.0 mol% Al_2O_3 ($d_{50} = 0.3 \mu\text{m}$) doped YSZ) are also plotted in these figures for comparison. Figures 11 to 13 are the relative densities of the selected materials calculated from the dimension change during hot pressing measured by a laser and their green densities. The densities of hot pressed samples were measured by image analysis using SEM. Disk samples with a diameter of 28.75mm and a thickness of about 2 mm in the green form followed the same temperature and pressure profiles first and then were used for hot pressing (T1, temperature up to 1380 °C, P2, pressure). Figure 11 shows that ultrafine (d_{50} particle size of 10-200 nm) $\alpha\text{-Al}_2\text{O}_3$ doped YSZ has a similar relative density with the micro (d_{50} particle size of 0.5-5 μm) $\alpha\text{-Al}_2\text{O}_3$ doped YSZ if calibrated with the green density difference. It is possible that the current hot pressing procedure did not reveal the advantage of ultrafine particles and/or the ultrafine particles were not well dispersed homogeneously in the YSZ matrix.

However, as shown in Figures 12 and 13, Samples #8 (1.5 mol% Mn_2O_3 doped YSZ), #10 (0.25 mol% $\alpha\text{-Al}_2\text{O}_3$ +0.25mol% Mn_2O_3 co-doped YSZ) and #12 (0.75 mol% $\alpha\text{-Al}_2\text{O}_3$ +0.75mol% Mn_2O_3 co-doped YSZ) showed improved relative density (up to 5% improvement after calibrated with the green density difference) with the same hot pressing procedure, as compared to E0616. Therefore, Samples #8, #10, #12 were selected as new electrolyte candidates and further studies on their sintering behaviors were conducted by hot pressing.

Various hot pressing procedures were selected to study the densification behaviors of selected compositions from the three doped YSZ series. The study was conducted on some electrolyte candidates of Samples #8 (1.5mol% Mn_2O_3 doped YSZ), #10 (0.25mol% $\alpha\text{-Al}_2\text{O}_3$ +0.25mol% Mn_2O_3 co-doped YSZ), #12 (0.75mol% $\alpha\text{-Al}_2\text{O}_3$ +0.75mol% Mn_2O_3 co-doped YSZ), and E0616 under T1 (1380 °C), P2 (3MPa); XT5 (1320 °C), XP7(10MPa, loading started at 1000 °C); T1, XP13 (7MPa); and XT5, XP12(10MPa; loading started at 900 °C). Figures 14 and 15 show the relative density and beta, respectively, as measured during hot pressing for the above four materials, including undoped YSZ as comparison. Under T1, P2 cycles, all doped YSZs show much higher relative densities than undoped YSZ (only 77%) (Figure 14) and Samples #8, #10, and #12 are higher than E0616. Sample #10 shows the highest relative density (89%). Sample #8 and #12 also show high relative densities. Under XT5, XP7 cycles (lower temperature but higher pressure) as shown in Figure 15, both Sample #8 and #12 have relative densities over 95% because of their low T_{peak} (~1200 °C) of the (dL/dT) curve but both Sample #10 and E0616 have relative densities only ~83% because of their high T_{peak} (~1300 °C). The results of Samples #10 and #12 under new hot pressing profiles, XP12 and XP13 with XT5 and T1, are also shown in Figures 14 and 15. Both Sample #10 and #12 had higher relative densities (~95%) under T1 and XP13 (higher pressure), compared to T1 and P2 (lower pressure), because of the use of a much higher pressure. The relative density was improved for Sample #10 (~5% relative density gain) when loading starting at 900 °C instead of at 1000 °C, as shown in Figure 15. However, the density of Sample #12 was decreased under XT5 and XP12 because the load might have been released too soon and because of its low $(\text{dL}/\text{dT})_{\text{max}}$ (0.0805, so that more time was needed to densify) compared to Sample #10 with a higher $(\text{dL}/\text{dT})_{\text{max}}$ (0.0935). The low T_{peak} and low $(\text{dL}/\text{dT})_{\text{max}}$ for Sample #12 meant that Sample #12

densification started earlier but needed more time. Sample #10 showed the opposite densification behavior so that it is very possible for both samples to reach the same relative density under XT5 and XP12 cycles.

The densities (porosities) of hot pressed samples were measured using SEM and image analysis (IA) techniques. These samples included some electrolyte candidates of Samples #8 (1.5 mol% Mn_2O_3 doped YSZ), #10 (0.25mol% $\alpha\text{-Al}_2\text{O}_3$ +0.25mol% Mn_2O_3 doped YSZ), #12 (0.75mol% $\alpha\text{-Al}_2\text{O}_3$ +0.75mol% Mn_2O_3 doped YSZ), and E0616 under T1 (1380 °C), P2 and XT5 (1320 °C), XP7 (loading started at 1000 °C). Figures 16 and 17 are the SEM photographs, respectively, and Table 3 summarizes the relative density and beta as measured during hot pressing, as well as the porosity measured by the IA technique for the above four materials, including undoped YSZ as comparison. The relative densities of the selected materials were calculated from the dimension change during hot pressing (diameter change measured by a laser and height change measured by an Instron machine) and their green densities. The porosities were measured from 6 images for each sample using the IA technique. As shown in Figures 16, 17 and Table 3, under T1, P2 cycles, all doped YSZs showed much higher relative densities than undoped YSZ (only 77%) and Samples #8, #10, and #12 were higher than E0616. Sample #10 showed the highest relative density (89%). Sample #8 and #12 also showed high relative densities. Under XT5, XP7 cycles (lower temperature but higher pressure) as shown in Figure 17 and Table 3, both Sample #8 and #12 had relative densities over 95% because of their low T_{peak} (~1200 °C) of the (dL/dT) curve but both Sample #10 and E0616 had relative densities of only about 83% because of their high T_{peak} (~1300 °C). The porosity measured by the IA technique and the relative density measured by the laser matched each other very well (the total was about 100%) for all the samples in this study. In T1, P2 profiles, 0.25mol% $\alpha\text{-Al}_2\text{O}_3$ +0.25mol% Mn_2O_3 doped YSZ performed better than E0616; in XT5, XP7 profiles, both 1.5 mol% Mn_2O_3 and 0.75mol% $\alpha\text{-Al}_2\text{O}_3$ +0.75mol% Mn_2O_3 doped YSZ performed better than E0616.

The roles of aluminum and manganese oxides on sintering and conductivity of yttria-stabilized zirconia as SOFC electrolyte have been extensively studied in the prior art, but, to our knowledge, none has used $\alpha\text{-Al}_2\text{O}_3$ + Mn_2O_3 to co-dope YSZ. Only Sakka *et al.*, added Al_2O_3 + Mn_3O_4 to 3mol% Y_2O_3 doped ZrO_2 (3YZP) to

- fabricate high-strain rate superplastic 3YTZ. Y. Sakka, T. Ishii, T. S. Suzuki, K. Morita, K. Hiraga, *Fabrication of high-strain rate superplastic yttria-doped zirconia polycrystals by adding manganese and aluminum oxides*, J. Euro. Ceram. Soc., 24(2004) 449-453. The solubility of Al_2O_3 in ZrO_2 grain is very low, only 0.5mol%.
- 5 Al_2O_3 can be dissolved in Y_2O_3 stabilized ZrO_2 at 1700 °C and cooled at 220 °C/hr. M. Miyayama, H. Yanagida, and A. Asada, *Effects of Al_2O_3 additions on resistivity and microstructure of yttria-stabilized zirconia*, Am. Ceram. Soc. Bull., 65[4] (1986) 660-664. The solubility of Al_2O_3 is about 0.1mol% when sintered at 1300 °C, so that the Al_2O_3 additions in this study are far beyond the Al_2O_3 solubility. H.
- 10 Bernard, *Sintered Stabilized Zirconia Microstructure and Conductivity*, Report CEA-R-5090, Commissariat a l'Energie Atomique, CEN-Saclay, France, 1981, P117. Guo *et al.*, have found that there are three forms of Al_2O_3 in existence in ZrO_2 . X. Guo and R. Z. Yuan, *Roles of alumina in zirconia-based solid electrolyte*, J. Mater. Sci., 30(1995) 923-931; X. Guo, C. Q. Tang, and R. Z. Yuan, *Grain*
- 15 *boundary ionic conduction in zirconia-based solid electrolyte with alumina addition*, J. Euro. Ceram. Soc., 15(1995) 25-32. They are: (1) a very small amount of Al_2O_3 is dissolved in ZrO_2 grains; (2) the surplus Al_2O_3 then forms Al_2O_3 particles, which are extensively situated intra- and intergranularly; (3) Al_2O_3 segregates at grain boundaries, and forms the crystal and the amorphous Al-rich grain boundary phases.
- 20 The amorphous phase contains impurities such as Si and Ca. However, manganese is soluble in YSZ, with a solubility limit between 5 mol% at 1000 °C and 15 mol% at 1500 °C. Mn stabilizes the cubic zirconia phase and therefore delays the cubic-to-tetragonal phase transformation. This was confirmed by SEM examination, as shown in Figure 18. Figure 18 shows the $\alpha\text{-Al}_2\text{O}_3$ particles on the surfaces of
- 25 0.5mol% $\alpha\text{-Al}_2\text{O}_3$ and 2.0 mol% $\alpha\text{-Al}_2\text{O}_3$ doped YSZ samples (Figure 18(b) and 18(c)) but none of Mn_2O_3 particles on the surface of 2.0mol% Mn_2O_3 doped YSZ samples (Figure 18(d)) after sintering pressurelessly at 1380 °C for 1hr. Figure 18 also shows that ZrO_2 particles sizes in doped YSZ samples are much larger than in the undoped YSZ sample (especially comparing Figure 18(d) showing 2.0mol%
- 30 Mn_2O_3 doped YSZ with Figure 18(a) showing undoped YSZ).

In the ZrO_2 system, the control step of densification is the bulk diffusion of Zr^{4+} which is affected by the defect structure of ZrO_2 . The defect structure of ZrO_2 is essentially controlled by the dopant when the dopant, such as Mn_2O_3 , is dissolved in

ZrO₂ in large amounts. The cation (*e.g.*, Zr⁴⁺) diffusion in the zirconia systems is much smaller than the oxygen diffusion so that the grain growth is controlled by the cation diffusion. It has been found that the grain growth rate increased by adding Al₂O₃ and Mn₂O₃ in YSZ as shown in Figure 18 and adding Al₂O₃ and Mn₃O₄ in 3YTZP. X. Guo and R. Z. Yuan, *Roles of alumina in zirconia-based solid electrolyte*, J. Mater. Sci., 30(1995) 923-931; Y. Sakka, T. Ishii, T. S. Suzuki, K. Morita, K. Hiraga, *Fabrication of high-strain rate superplastic yttria-doped zirconia polycrystals by adding manganese and aluminum oxides*, J. Euro. Ceram. Soc., 24(2004) 449-453. Therefore, it is concluded that cation diffusion is enhanced by adding Al₂O₃ and/or Mn₂O₃ (Mn₃O₄) to zirconia. In fact, the Al₂O₃ addition has a dual effect on grain growth. First, the intergranular Al₂O₃ particles pin grain boundaries; second, the Al₂O₃ segregated at grain boundaries can improve the mobility of the boundaries because the Al₂O₃ segregation at grain boundaries may increase the grain-boundary diffusion coefficient. The above experimental results demonstrate that the sum of these two effects of Al₂O₃ is to promote grain growth. Therefore, adding Al₂O₃ and Mn₂O₃ enhance the densification of YSZ. The decrease in sintering temperature with Al₂O₃ doping may be also ascribed to a liquid-phase sintering mechanism. Al₂O₃ and the impurities (such as SiO₂) in TZ-8Y can form a low temperature liquid phase during sintering which improve the sinterability of YSZ. M. J. Verkerk, A. J. A. Winnubst, and B. A. J. Burggraaf, *Effect of impurities on sintering and conductivity of yttria-stabilized zirconia*, J. Mater. Sci., 17(1982) 3113-3122.

In this study, the densities of hot pressed samples were lower than the densities of free sintered samples at the same temperature because of the constraint from the hot pressing fixture (dense zirconia plates on both surfaces of the samples here) which would reduce the shrinkage and densification of both undoped and doped YSZs if the hot pressing load (such as the load used) was not high enough to overcome this reduction in shrinkage.

Conductivity of undoped YSZ and doped YSZ

The electronic conductivities of Sample #0 (pure YSZ), #4, #9, and #13 (with the highest dopant level, 2.0 mol% in each YSZ series in this study) were

measured in both air and forming gas at 800, 900, and 1000 °C by the two-probe technique. The results are summarized in Table 4. Table 4 also shows the total conductivity of these samples. It has been found that doping with Al_2O_3 , Mn_2O_3 , and $\text{Al}_2\text{O}_3+\text{Mn}_2\text{O}_3$ does not increase the electronic conductivity of YSZ (in fact, the electronic conductivity decreases with Mn doping confirming earlier statements in the literature). The electronic conductivities of doped YSZ are lower than pure YSZ in both air and forming gas. Therefore, the OCV of cells using the doped YSZ as the electrolytes will be as good as using undoped YSZ as the electrolyte. Verkerk *et al.*, have found that 0.78mol% Al_2O_3 addition has a negative influence on both the bulk and grain-boundary conductivity of YSZ, and Mn doping was always found to reduce the bulk conductivity of YSZ but responsible for slow conductivity decay (> 1000 hrs) at high temperature (850-1000 °C). M. J. Verkerk, A. J. A. Winnubst, and B.A. J. Burggraaf, *Effect of impurities on sintering and conductivity of yttria-stabilized zirconia*, J. Mater. Sci., 17(1982) 3113-3122; C. C. Appel, N. Bonanos, A. Horsewell, and S. Linderorth, *Ageing behaviour of zirconia stabilised by yttria and manganese oxide*, J. Mater. Sci., 36(2001) 4493-4501; J. H. Kim and G. M. Choi, *Electrical conductivity of zirconia-Mn oxide mixture*, Materials Research Society Symposium - Proceedings, v 548, 1999, p 611-616. Proceedings of the 1998 MRS Fall Meeting - Symposium 'Solid State Ionics V', Nov 28-Dec 3, 1998, Boston, MA.

Table 3. Relative Density of Evaluated Electrolyte Materials (with equi-molar α - $\text{Al}_2\text{O}_3 + \text{Mn}_2\text{O}_3$)

Sample ID	Undoped YSZ	E0616		E0704		E0704		E0704	
Composition	TZ-8Y	1.0 mol%Al		1.5 mol%Mn		0.5 mol%Al+Mn		1.5 mol%Al+Mn	
T & P Profiles	T1, P2	T1, P2	XT5, XP7	T1, P2	XT5, XP7	T1, P2	XT5, XP7	T1, P2	XT5, XP7
Porosity (%) by IA	22.6±5.5	12.4±1.1	16.6±2.2	9.8±3.1	5.7±1.3	11.1±1.7	12.5±2.5	11.6±3.6	6.3±0.9
Relative Density (%) by laser *	77	83	83	88	96	89	85**	86	97
*Green density calibrated with E0616							** Average in two samples		

Table 4. Electronic conductivities of doped YSZ samples (with equi-molar α -Al₂O₃ + Mn₂O₃)

		Air:				5%H ₂ -N ₂		
T		800	900	1000		800	900	1000
1000/T		0.000932	0.00085	0.00079		0.000932	0.000852515	0.0007855
PO ₂ /atm (on one side of disc)		0.024143	0.02903	0.03391		4.6E-20	5.52991E-20	2.778E-19
PO ₂ /atm (on the other side)		0.21	0.21	0.21		4.00E-19	4.00E-19	4.00E-19
#13 (1.0mol% Al ₂ O ₃ +1.0mol%Mn ₂ O ₃ doped YSZ)	$\sigma(e)$	1.47E-05	3.46E-05	1.24E-04		5.42E-05	8.06E-05	9.50E-04
	$\sigma(t)$	3.11E-02	3.58E-02	6.48E-02		1.96E-02	3.45E-02	5.16E-02
#4(2mol% Al ₂ O ₃ doped YSZ)	$\sigma(e)$	8.79E-05	1.20E-04	1.45E-04		4.86E-05	1.22E-04	2.86E-04
	$\sigma(t)$	2.03E-02	5.57E-02	7.38E-02		7.87E-03	9.05E-03	Wire broken
#9(2mol% Mn ₂ O ₃ doped YSZ)	$\sigma(e)$	4.86E-05	1.10E-04	2.93E-04		2.59E-05	1.17E-04	6.60E-04
	$\sigma(t)$	2.23E-02	3.71E-02	4.96E-02		2.01E-02	3.64E-02	5.09E-02
#0 (YSZ)	$\sigma(e)$	3.46E-03	9.00E-03	1.86E-02		1.84E-04	3.09E-04	Wire broken
	$\sigma(t)$	3.81E-02	6.53E-02	8.87E-02		2.86E-02	1.65E-02	Wire broken
$\sigma(e)$ -electronic conductivity								
$\sigma(t)$ -total conductivity								
Unit: S.cm-1								

Open circuit voltage of symmetrical cells with undoped YSZ and doped YSZ
5 as electrolyte

The open circuit voltage (OCV) of symmetric cells using undoped and doped YSZ as the electrolytes were measured using humidified hydrogen (3% H₂O) as the fuel and air as the oxidant. Undoped YSZ (Sample #0) and samples with the highest dopant level (2 mol%) in the three series (Sample #4, #9 and #13) were selected for
10 this study. Samples with a diameter of 30 mm and a thickness of 1 mm were separately sintered pressurelessly at 1380 °C for 1 hr for Sample #0, 1330 °C for 1 hr for Sample #4, 1275 °C for 1 hr for both Sample #9 and #13, based on their dilatometry curves. A relative density of 99% for Sample #0, 97% for Sample #4, 99% for Sample #9, and 98% for Sample #13, respectively, was achieved after
15 sintering. A platinum paste was applied on both surfaces of the sintered disks to get symmetric cells and then the open circuit voltages of the cells were measured in 800, 900, and 1000 °C using humidified hydrogen (3% H₂O) as the fuel and air as the oxidant. The results are shown in both Table 5 and Figure 19. Data from thermodynamic calculation (theoretical OCV based on H₂+3%H₂O fuel and air) and
20 1.0 mol% Mn+Co co-doped electrolyte from a previous study are included in Table 5 and Figure 19 for comparison. As shown in Table 5 and Figure 19, both undoped

YSZ (Sample #0) and doped YSZs (Samples #4, #9, and #13) in this study showed very high OCV under the testing conditions, which are very close to the theoretical OCV. The decrease of OCV with an increase in temperature is due to purely thermodynamic behavior, not caused by the reduction of the dopant, such as, for example, 1.0 mol% Mn+Co co-doped electrolyte, causing a short circuit. All the doped YSZs in this study are good electrolyte materials based on the above results.

Table 5. Open circuit voltages (OCV, Volt) of symmetrical cells using undoped and doped YSZ (with equi-molar α -Al₂O₃+ Mn₂O₃) as the electrolytes with humidified H₂ (3%H₂O) as the fuel and air as the oxidant.

Temp.(C)	Open Circuit Voltage (V)					
	Theoretical OCV	Undoped YSZ	2 mol% α -Al ₂ O ₃ doped YSZ	2 mol% Mn ₂ O ₃ doped YSZ	2 mol% α -Al ₂ O ₃ + Mn ₂ O ₃ co-doped YSZ	1mol%Mn+Co co-doped YSZ
800	1.101	1.117	1.101	1.069	1.094	0.94
900	1.085	1.1	1.081	1.065	1.076	0.8
1000	1.069	1.079	1.058	1.053	1.059	0.73

Conclusions

1. The sintering temperature and densification behavior of 8 mol% yttria stabilized zirconia (YSZ) can be significantly reduced and modified by adding one or two ultrafine cation dopants in a conventional ceramic process.

2. A small amount of ultrafine- α -Al₂O₃, Mn₂O₃ doping, and α -Al₂O₃ + Mn₂O₃ co-doping can significantly reduce the peak temperature of the (dL/dT) curve and the maximum shrinkage rate of YSZ. The peak temperature (T_{peak}) of pure YSZ can be reduced over 207 °C with 0.5mol% α -Al₂O₃+1.5mol% Mn₂O₃ co-doping and the maximum shrinkage rate of YSZ can be reduced from 0.11 to 0.08, dilatometry dL/dT full width half maximum (FWHM) can be increased over 100 °C with 2.0mol% Mn₂O₃ doping.

3. A small amount of Al_2O_3 , Mn_2O_3 doping, and $\alpha\text{-Al}_2\text{O}_3\text{+Mn}_2\text{O}_3$ co-doping do not increase the electronic conductivity of YSZ, such as, for example, Tosoh TZ-8Y. Therefore, the open circuit voltage of cells using the doped YSZ as the electrolytes will be as good as using undoped YSZ.

- 5 4. It becomes possible to densify the YSZ electrolyte at 1150~1200 °C with $\alpha\text{-Al}_2\text{O}_3\text{+Mn}_2\text{O}_3$ co-doping.

The teachings of all patents, published applications and references cited herein are incorporated by reference in their entirety.

EQUIVALENTS

- 10 While this invention has been particularly shown and described with references to example embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made therein without departing from the scope of the invention encompassed by the appended claims.

CLAIMS

What is claimed is:

1. A method for forming an electrolyte of a solid oxide fuel cell, comprising the steps of:
 - 5 a) combining an yttria-stabilized zirconia powder with α -Al₂O₃ having a d₅₀ particle size in a range of between about 10 nm and about 200 nm and Mn₂O₃ to form an electrolyte precursor composition; and
 - b) sintering the electrolyte precursor composition to thereby form the electrolyte.
- 10 2. The method of Claim 1, wherein the α -Al₂O₃ and Mn₂O₃ are present in the electrolyte precursor composition in an amount in a range of between about 0.25 mol% and about 5 mol%.
3. The method of Claim 2, where in the α -Al₂O₃ and Mn₂O₃ is present in the electrolyte precursor in an amount of about 2 mol%.
- 15 4. The method of Claim 3, wherein the composition of the yttria-stabilized zirconia powder includes at least one of: yttria in an amount between about 3% and about 10 mol% of the powder; and zirconia in an amount between about 97 mol% and about 90 mol% of the powder.
5. The method of Claim 4, wherein yttria is present in the yttria-stabilized
20 zirconia powder in an amount of about 8 mol%.
6. The method of Claim 5, wherein the d₅₀ particle size of the yttria-stabilized zirconia powder is in a range of between about 0.05 μ m and about 1 μ m.
7. The method of Claim 1, wherein the ratio of α -Al₂O₃:Mn₂O₃ is in a range of between about 0.25:1 to about 1:0.25.
- 25 8. The method of Claim 1, wherein the d₅₀ of the α -Al₂O₃ is about 50 nm.
9. The method of Claim 1, wherein the specific surface area of α -Al₂O₃ is in a range of between about 5 m²/g and about 30 m²/g.
10. The method of Claim 9, wherein the specific surface area of the α -Al₂O₃ is about 17 m²/g.

11. The method of Claim 1, wherein the d_{50} of the Mn_2O_3 is in a range of between about 50 nm and about 400 nm.
12. The method of Claim 11, wherein the d_{50} of the Mn_2O_3 is about 200 nm.
13. The method of Claim 12, wherein the specific surface area of the Mn_2O_3 is in
5 a range of between about $10\text{ m}^2/\text{g}$ and about $50\text{ m}^2/\text{g}$.
14. The method of Claim 13, wherein the specific surface area of Mn_2O_3 is about $32\text{ m}^2/\text{g}$.
15. The method of Claim 1, wherein the d_{50} of the yttria-stabilized zirconia (YSZ) powder is in a range of between about 50 nm and about 1000 nm.
- 10 16. The method of Claim 15, wherein the d_{50} of the YSZ is about 250 nm.
17. The method of Claim 16, wherein the specific surface area of the YSZ is in a range of between about $5\text{ m}^2/\text{g}$ and about $30\text{ m}^2/\text{g}$.
18. The method of Claim 17, wherein the specific surface area of the YSZ is about $13\text{ m}^2/\text{g}$.
- 15 19. An electrolyte of a solid oxide fuel cell that is doped with $\alpha\text{-Al}_2\text{O}_3$ and Mn_2O_3 .
20. A solid oxide fuel cell that includes an electrolyte component doped with $\alpha\text{-Al}_2\text{O}_3$ and Mn_2O_3 .

1/21

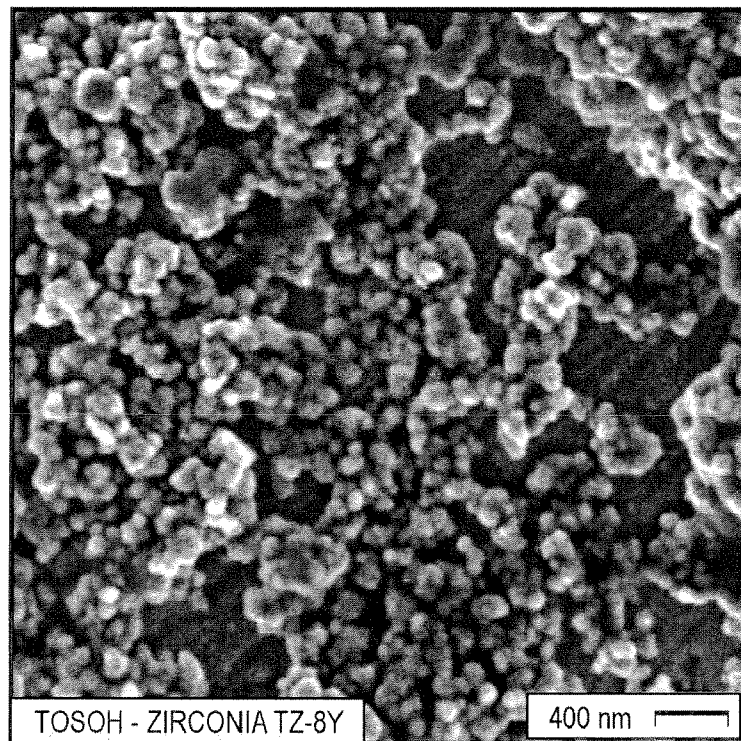


FIG. 1

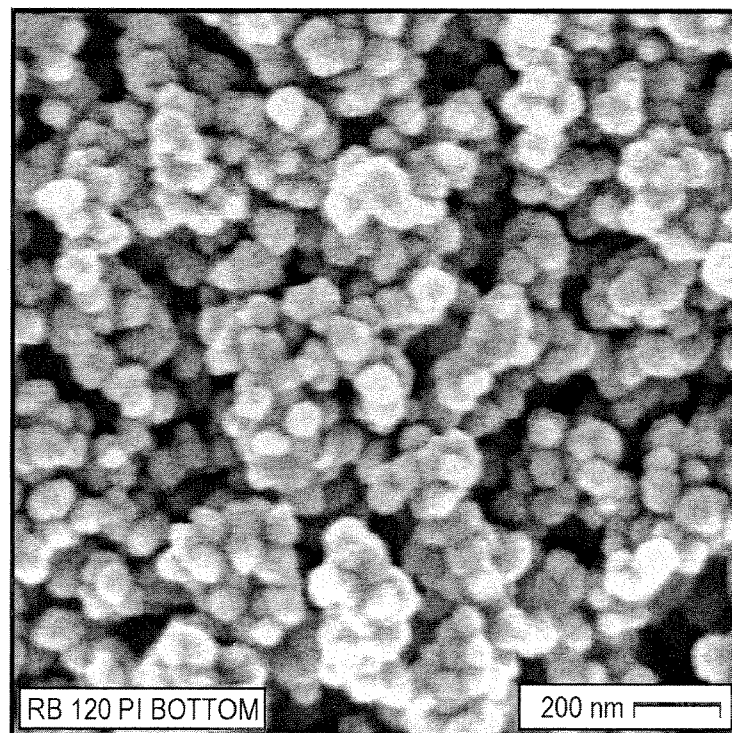


FIG. 2

2/21

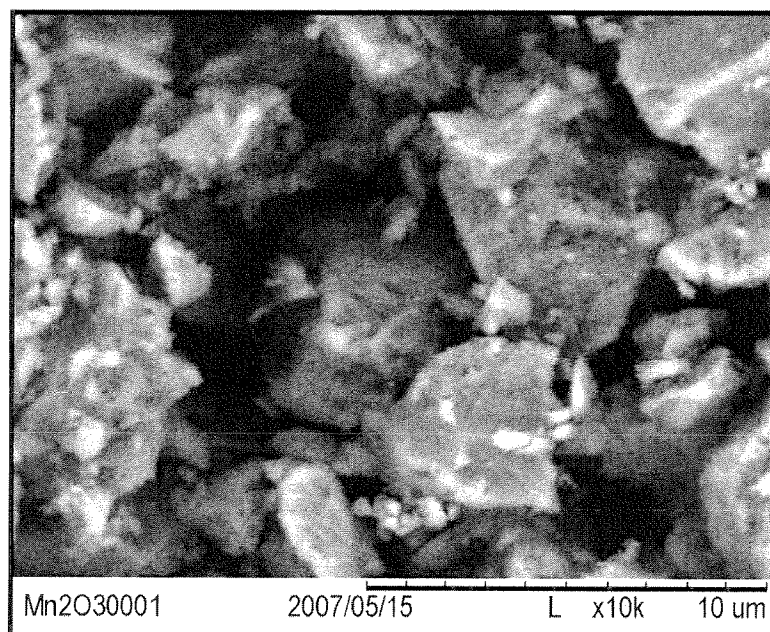


FIG. 3A

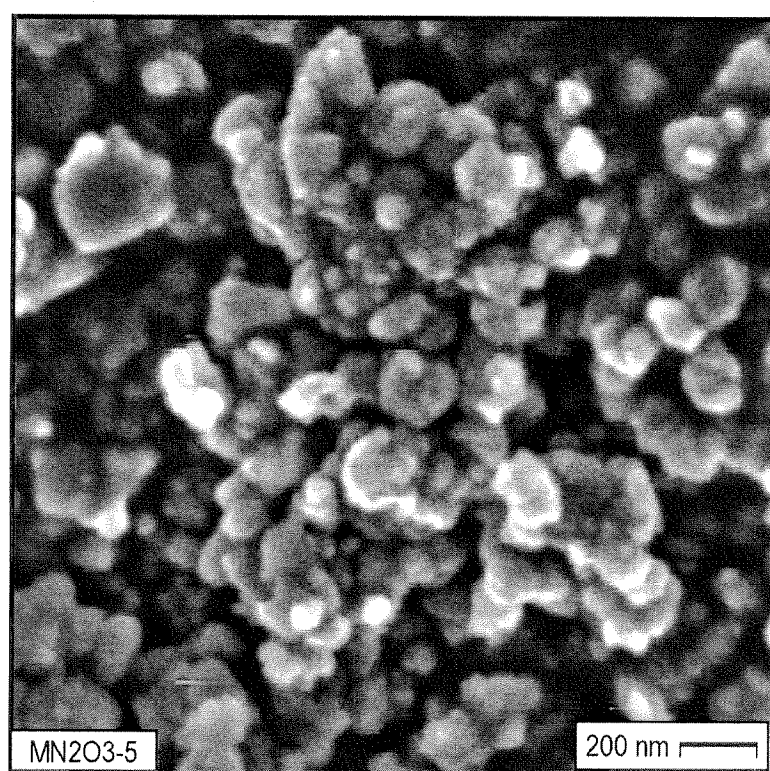


FIG. 3B

3/21

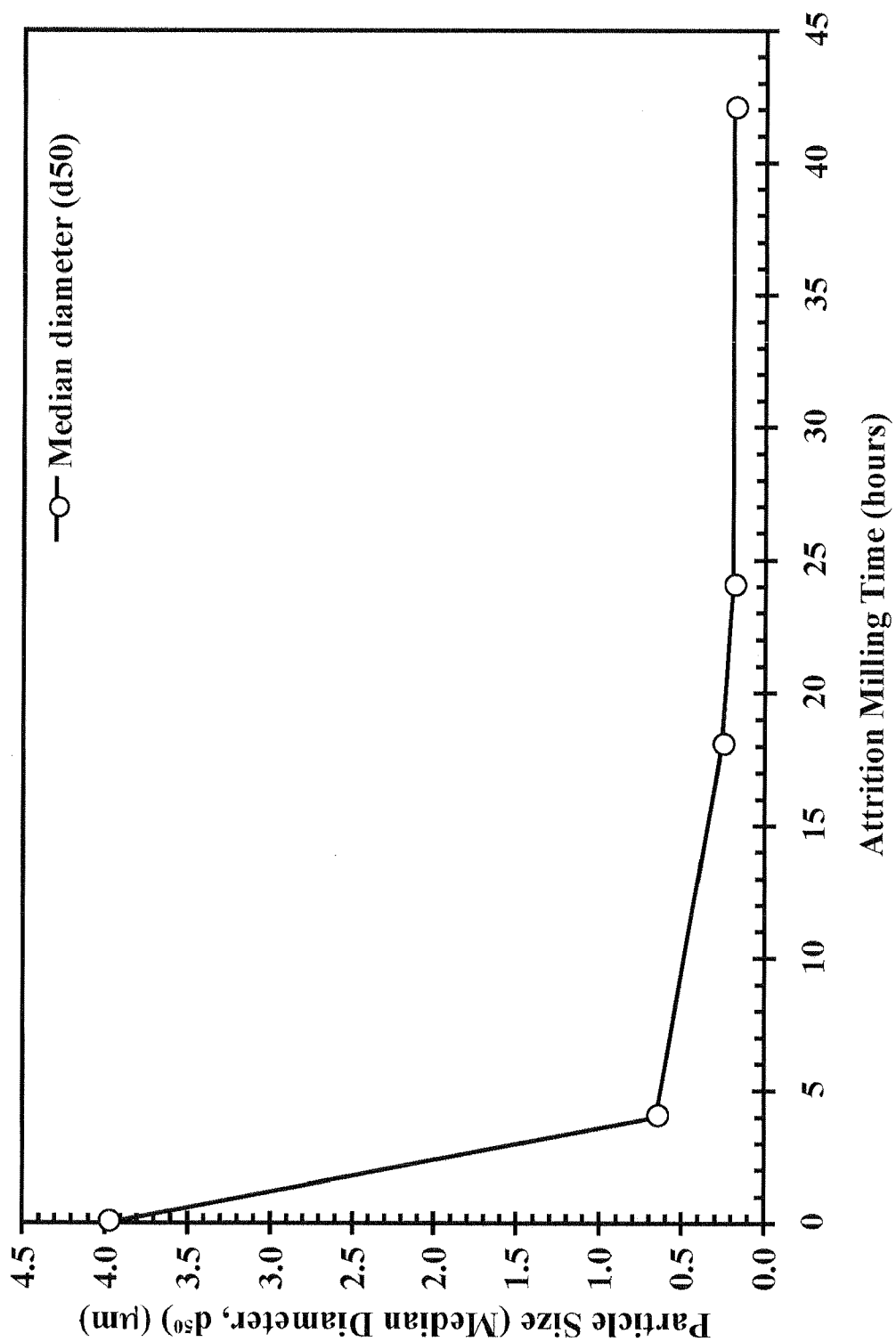


FIG. 4A

4/21

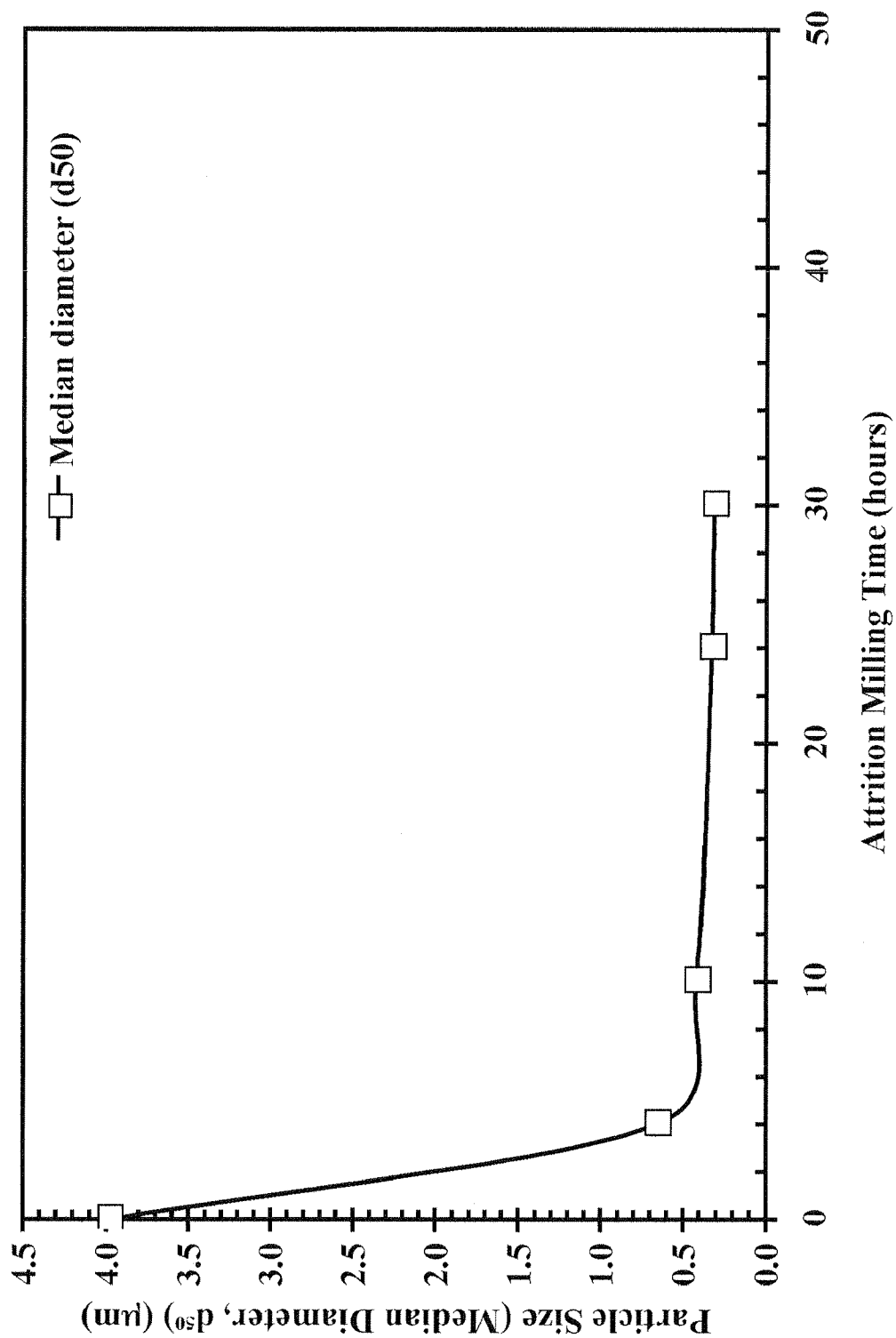


FIG. 4B

5/21

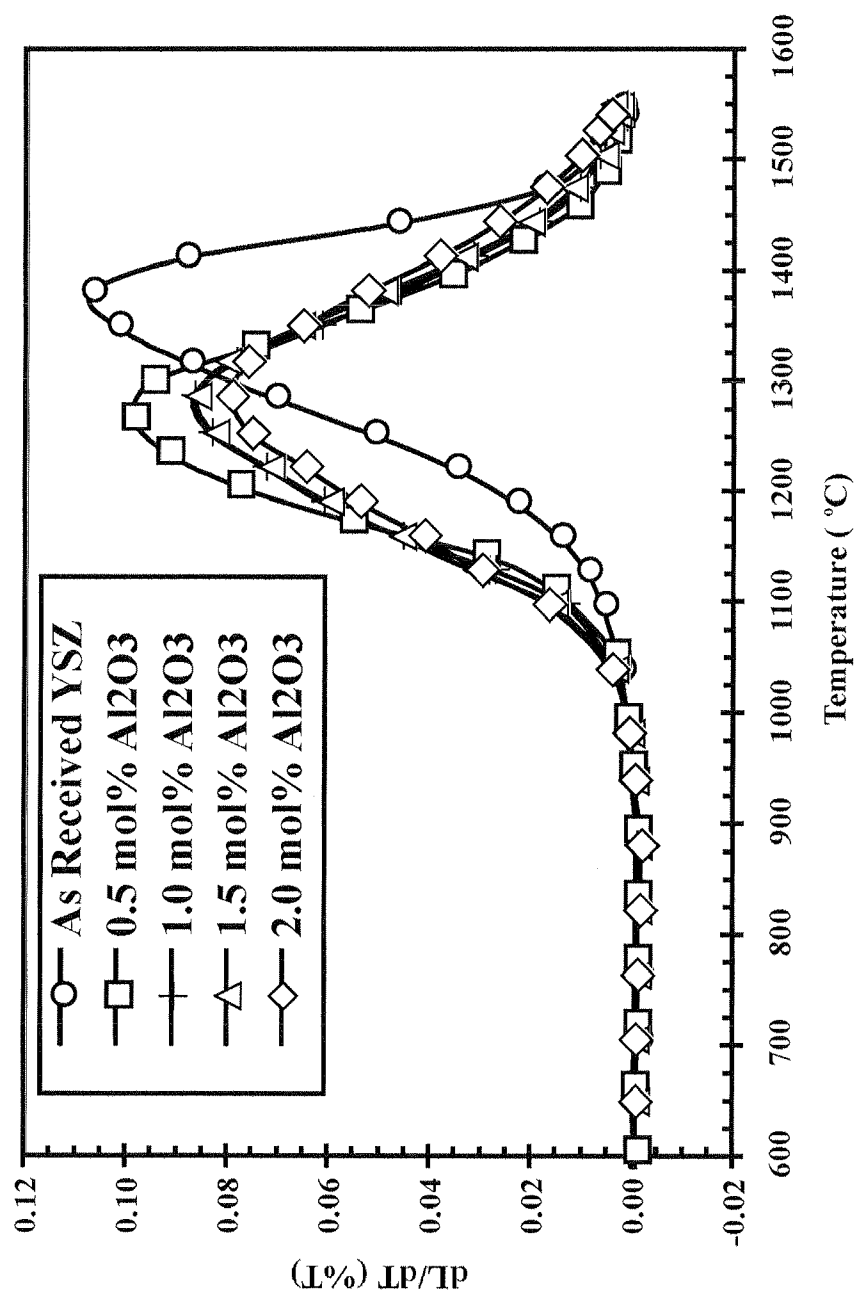


FIG. 5

6/21

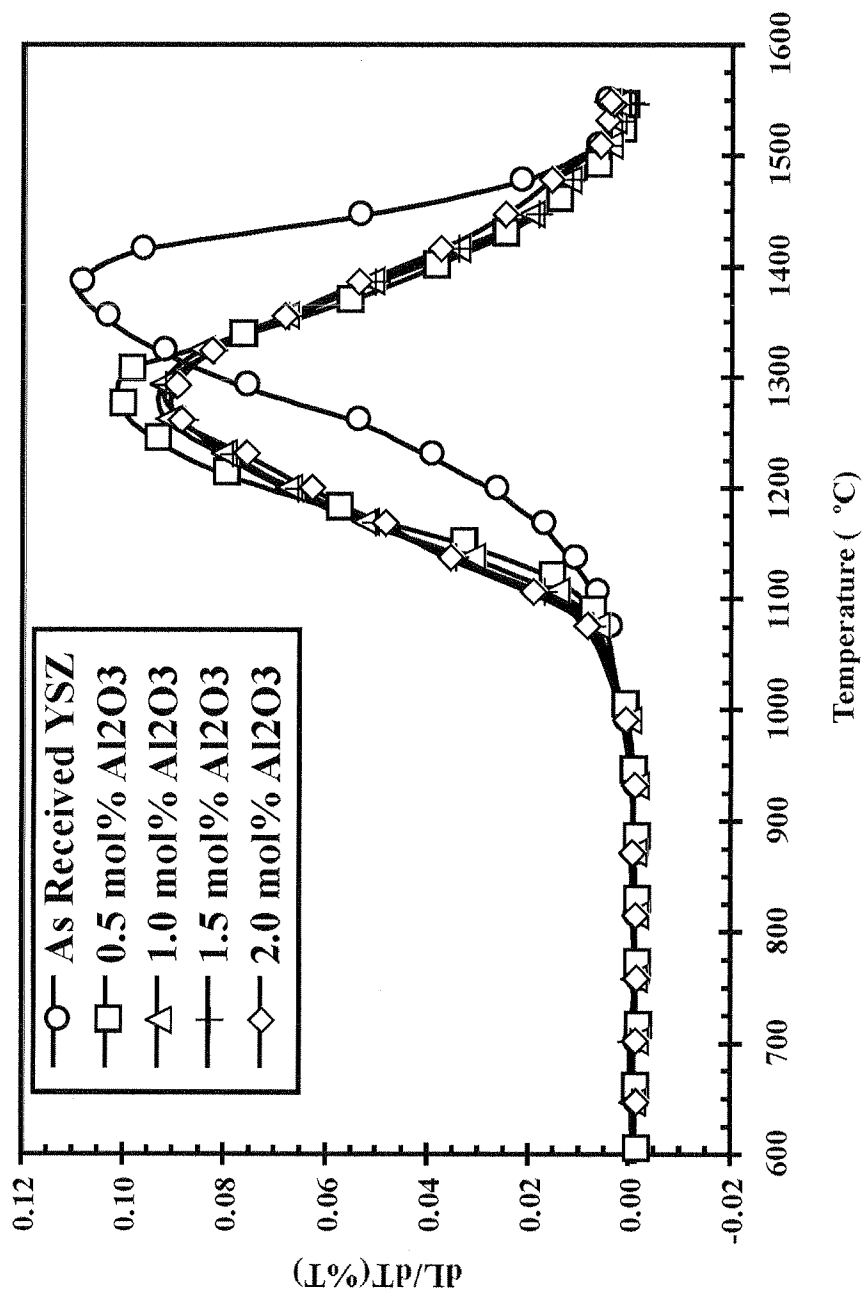


FIG. 6

7/21

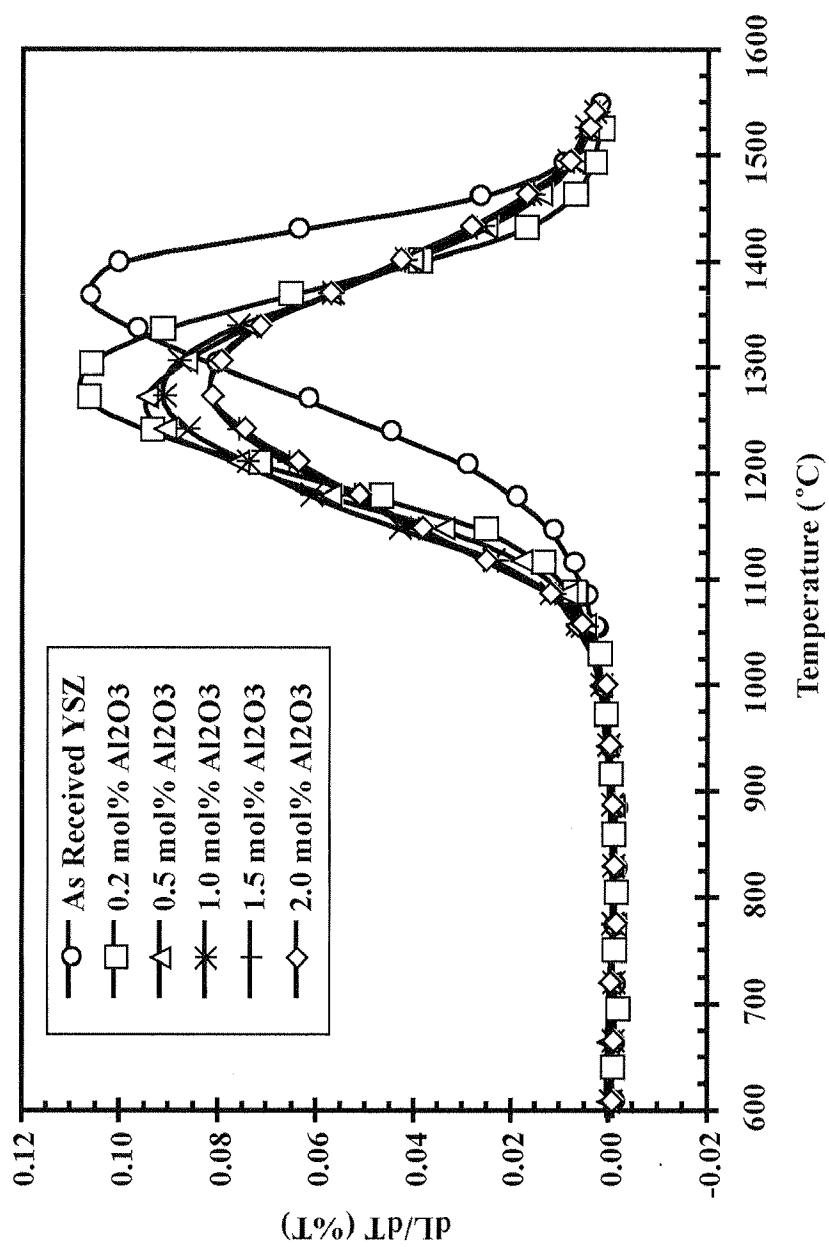


FIG. 7

8/21

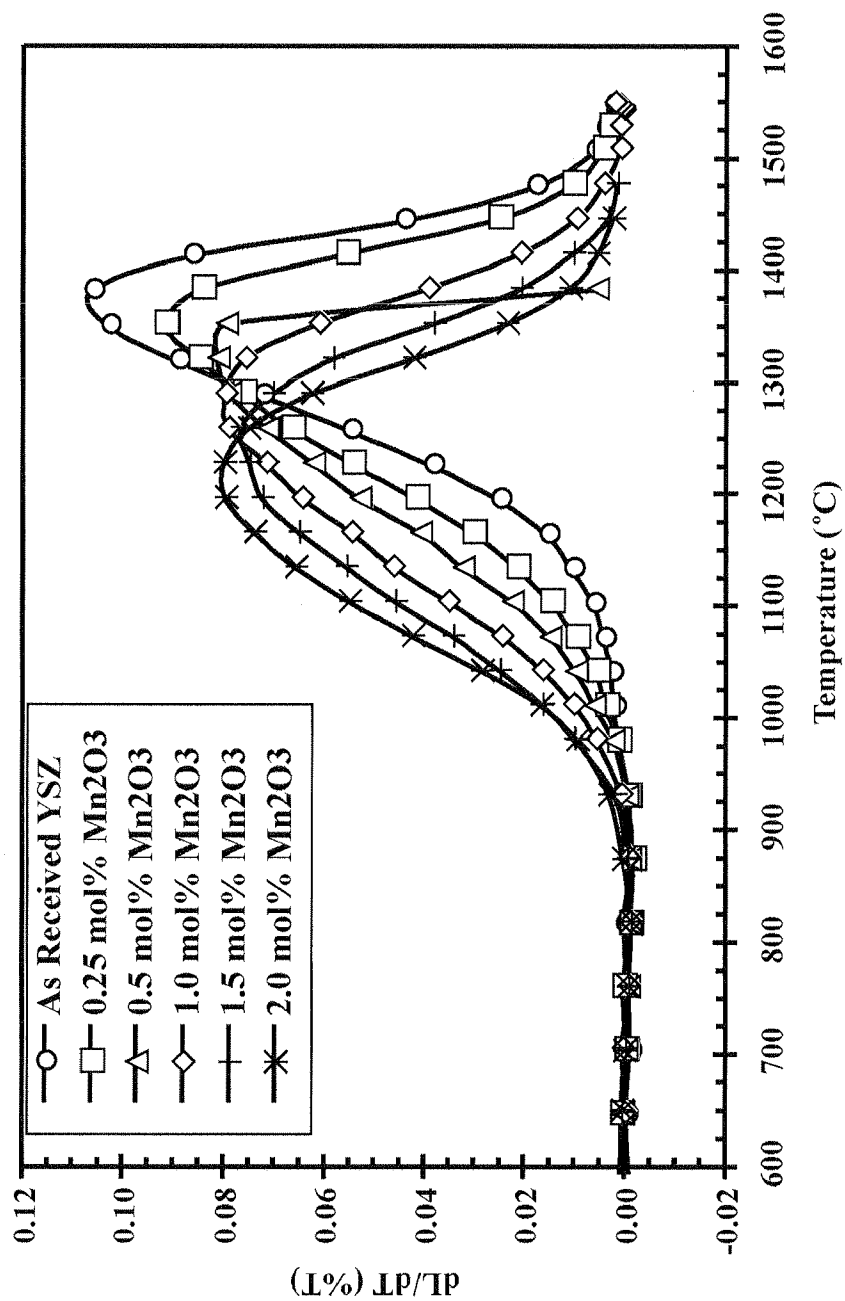


FIG. 8

9/21

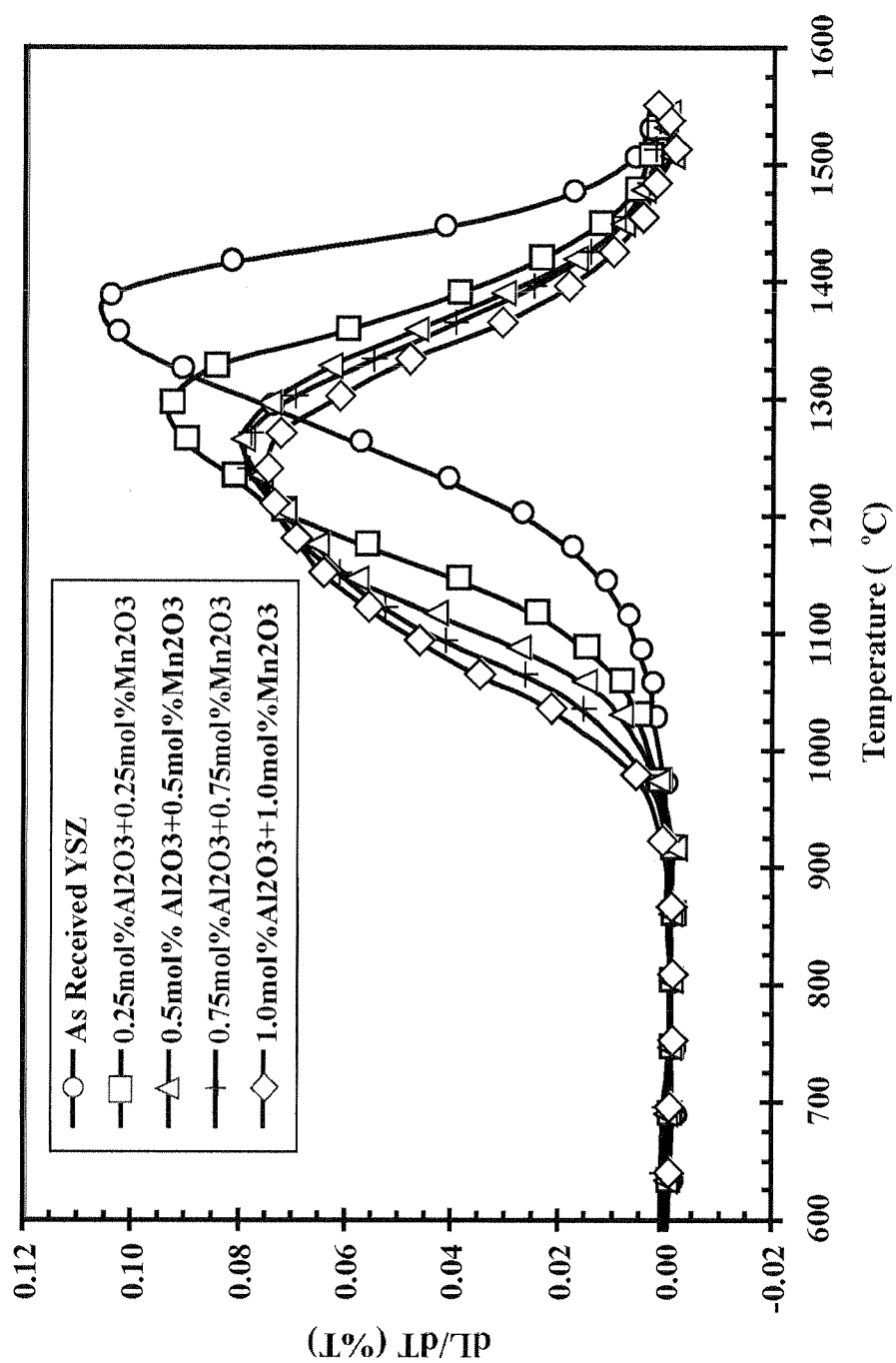


FIG. 9A

10/21

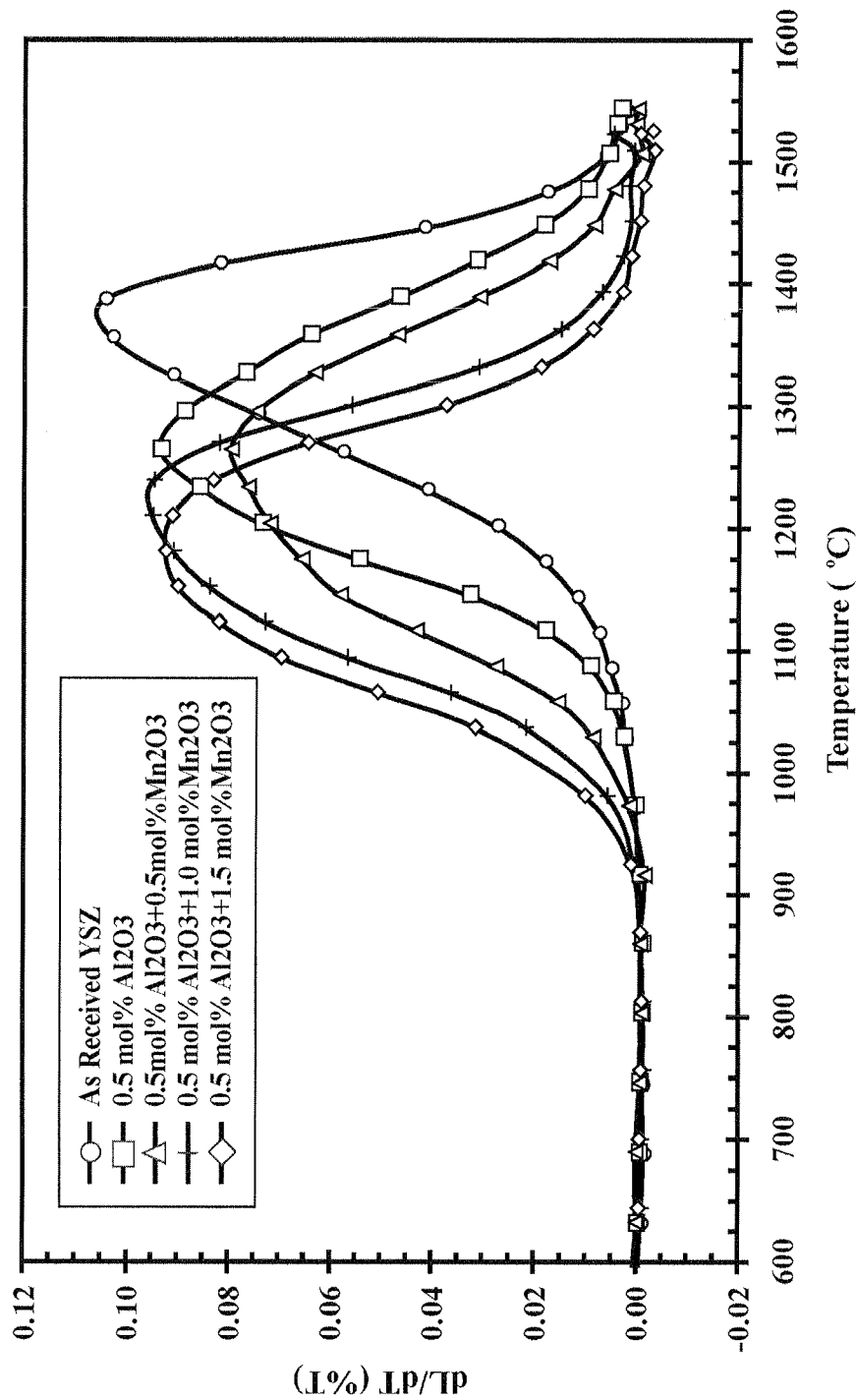


FIG. 9B

11/21

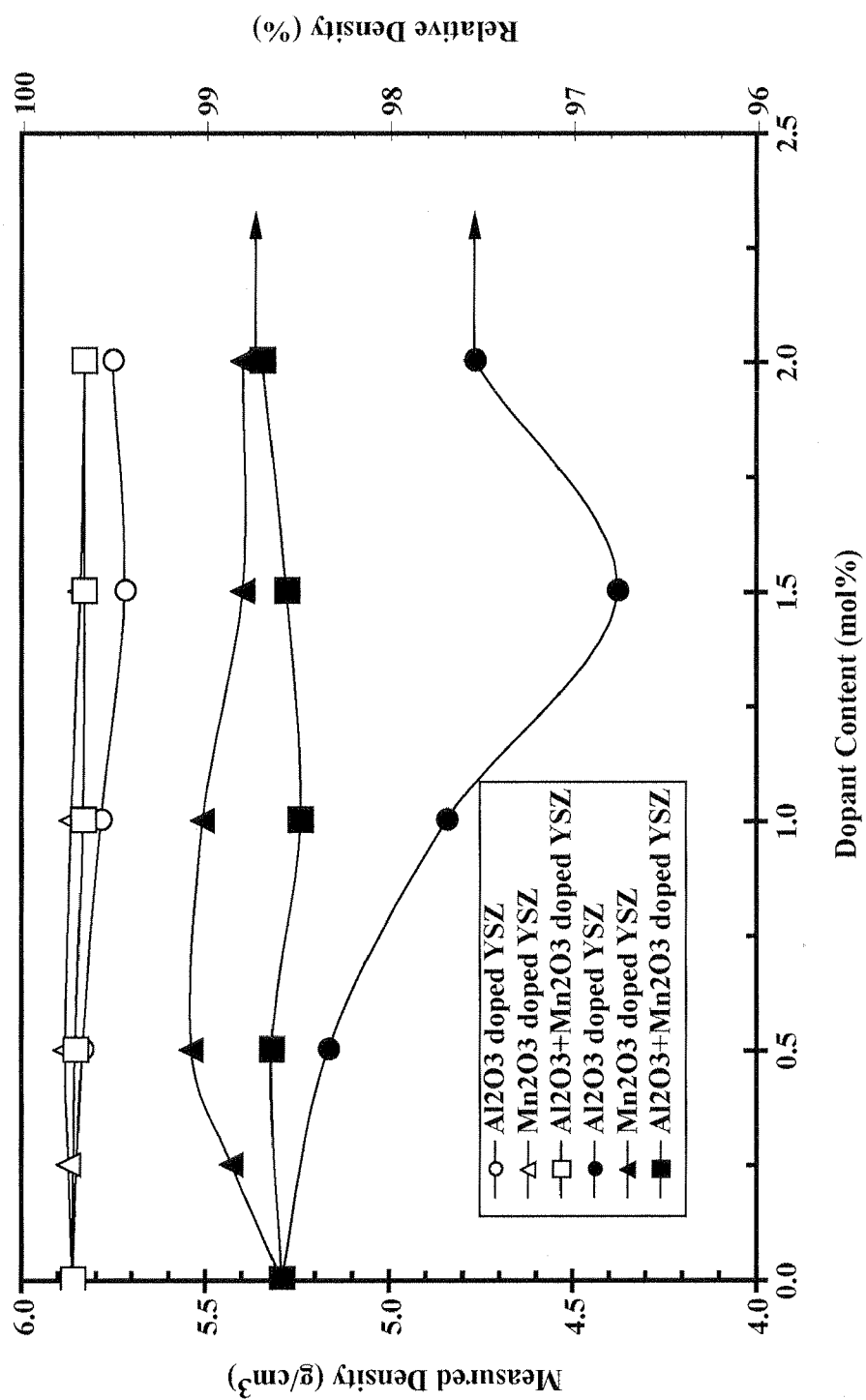


FIG. 10

12/21

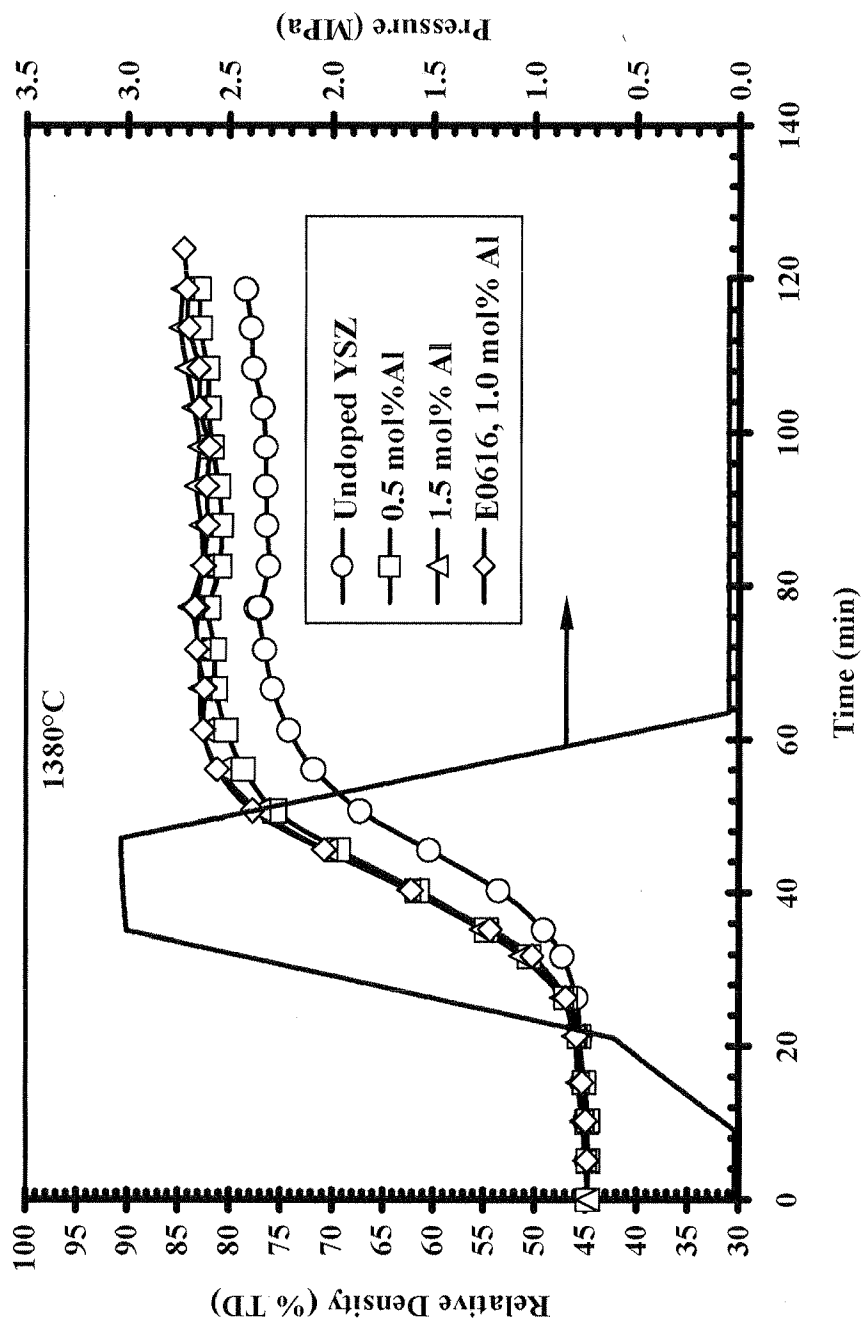


FIG. 11

13/21

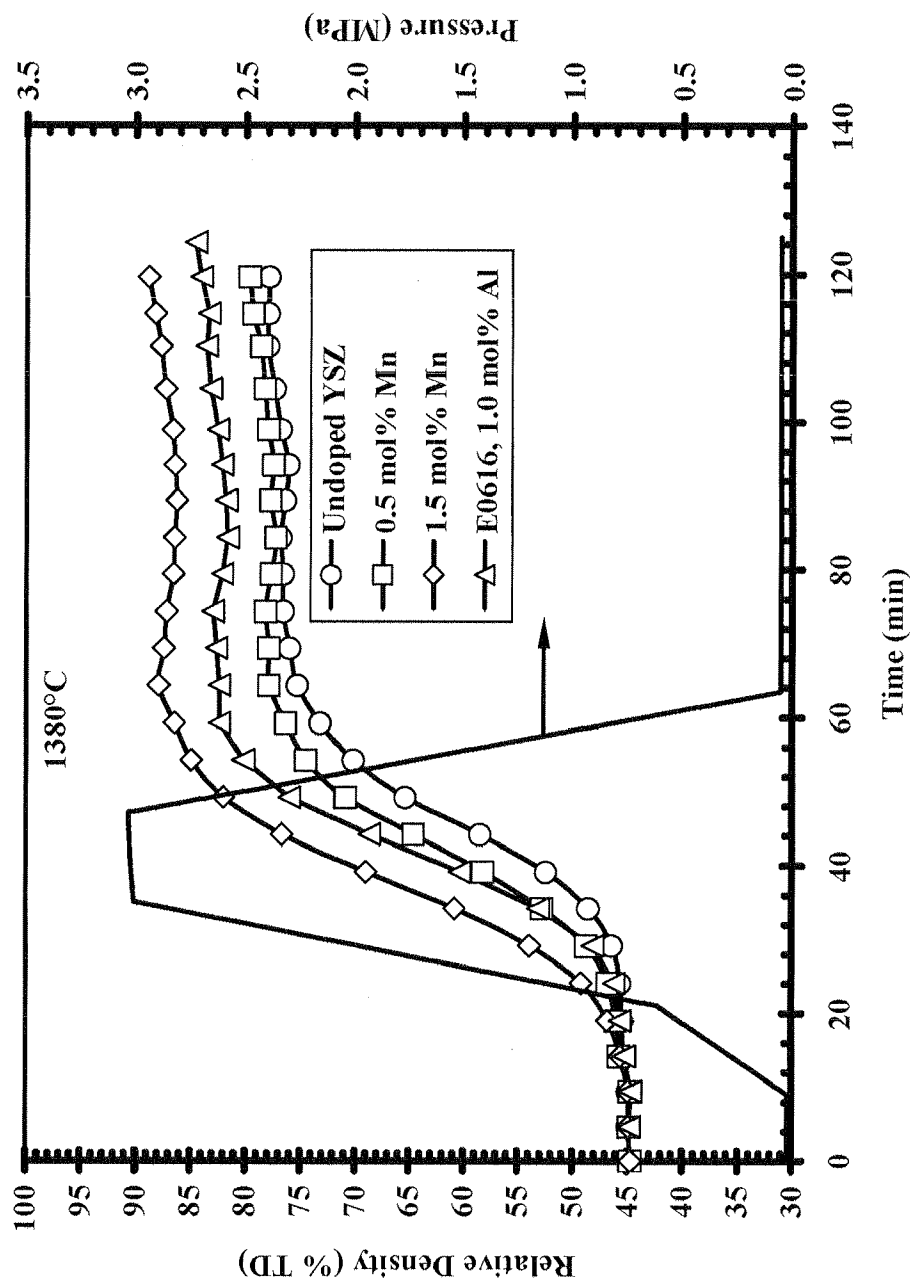


FIG. 12

14/21

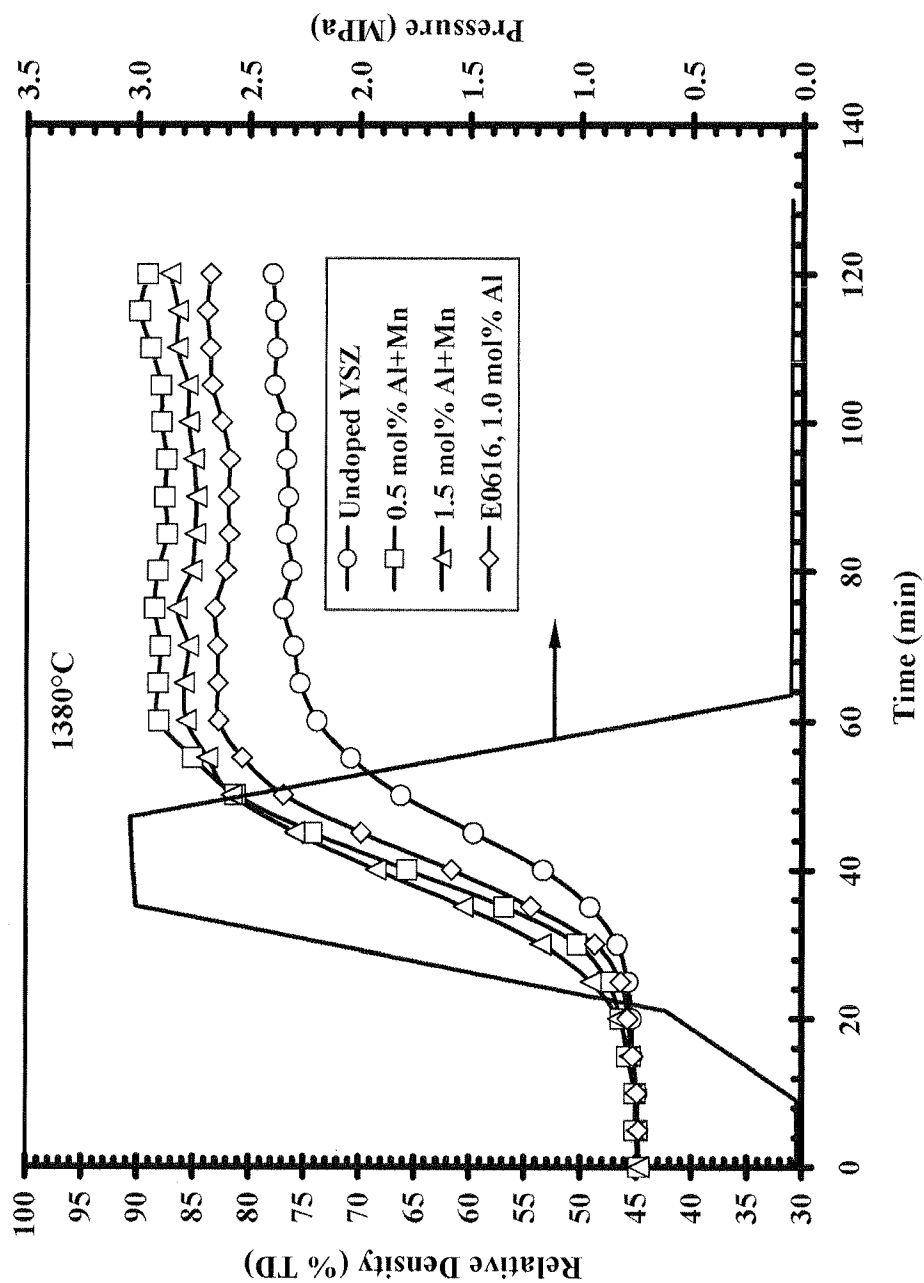


FIG. 13

15/21

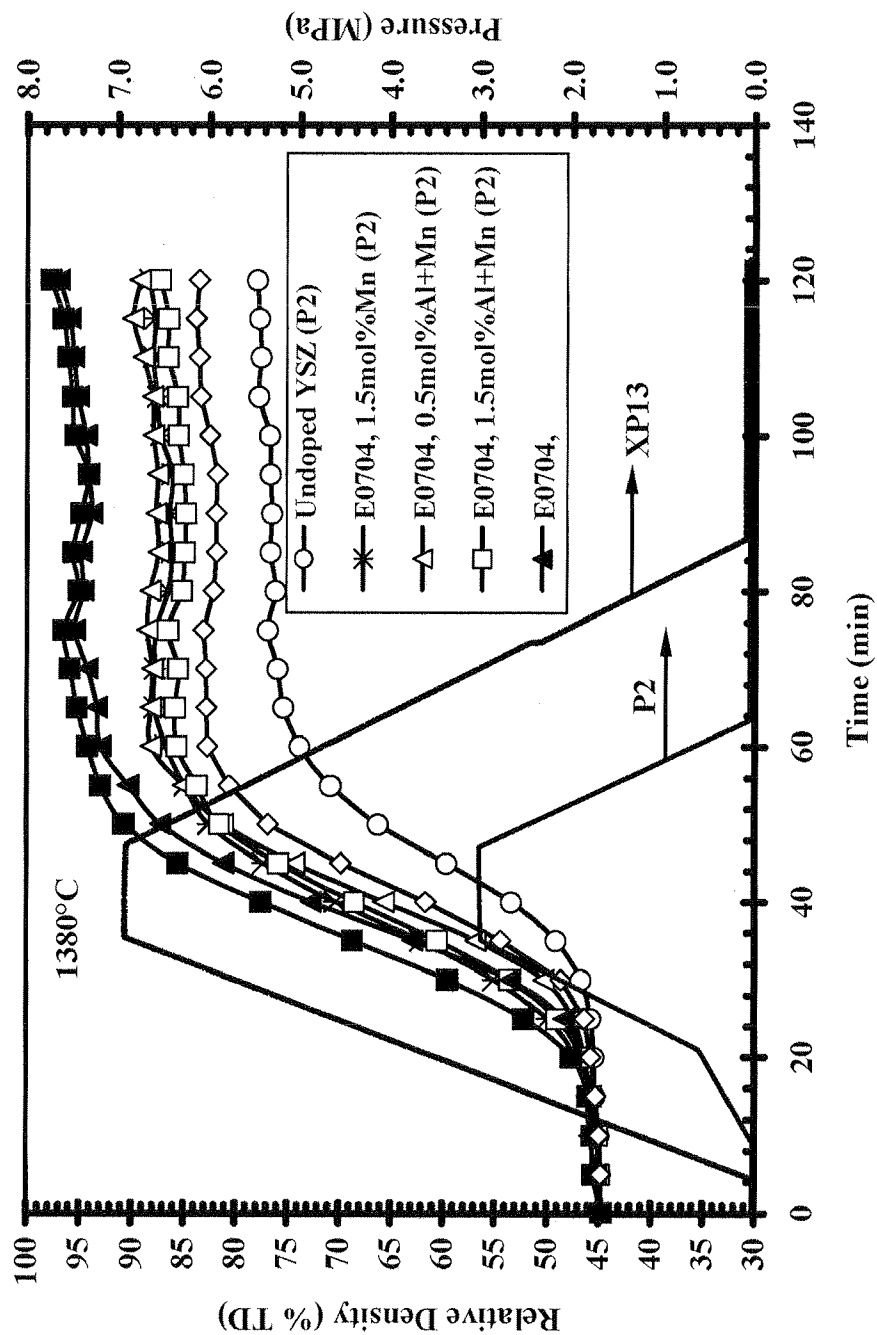


FIG. 14

16/21

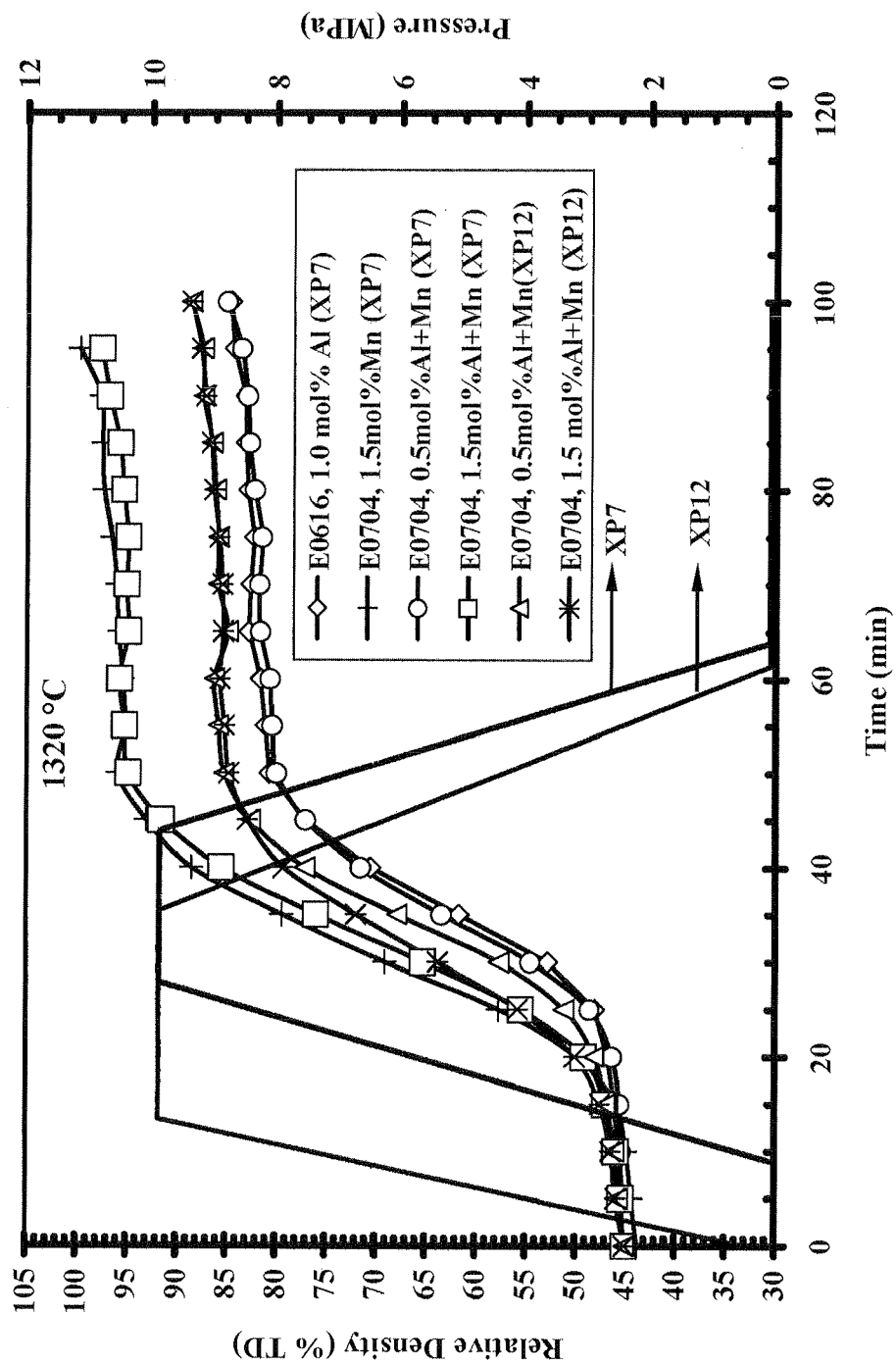


FIG. 15

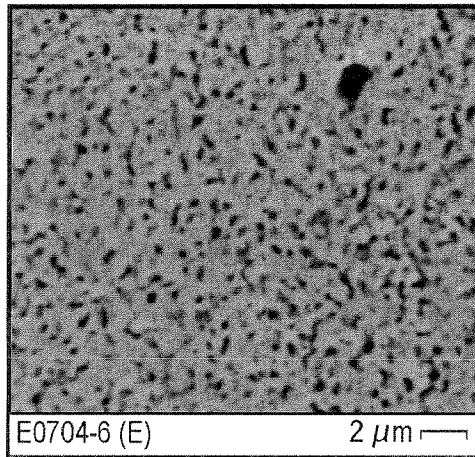


FIG. 16A

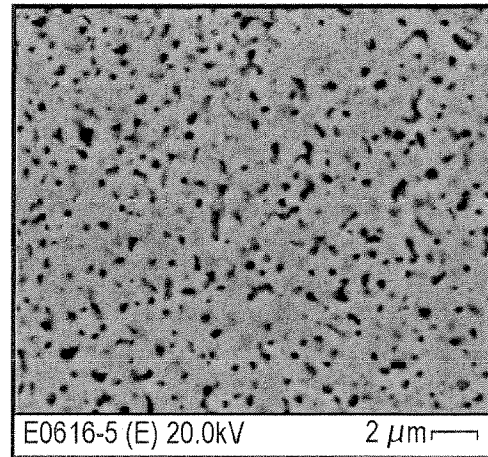


FIG. 16B

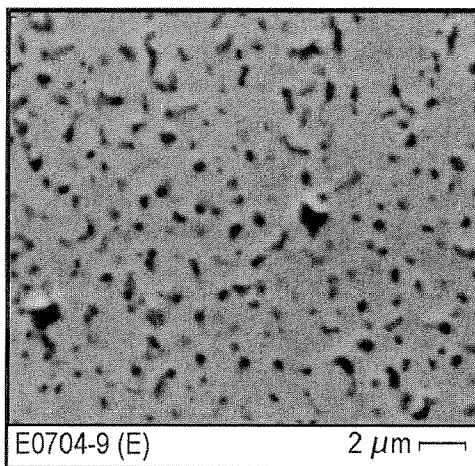


FIG. 16C

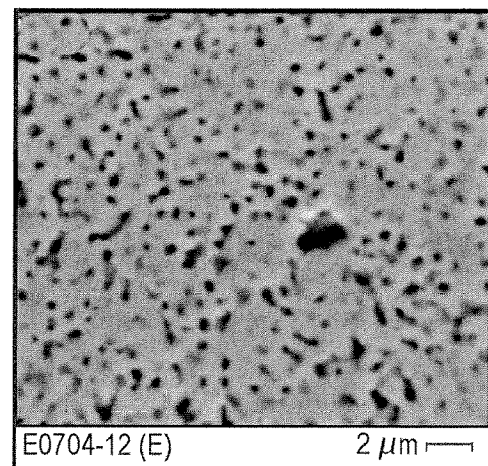


FIG. 16D

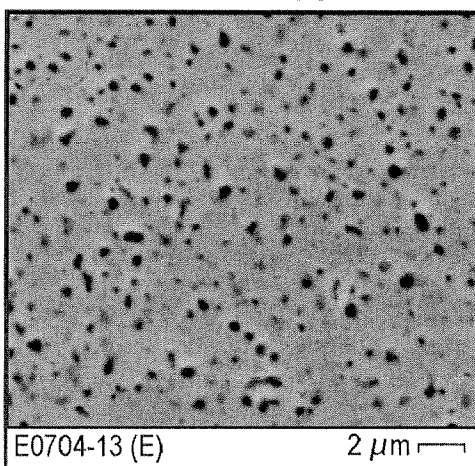


FIG. 16E

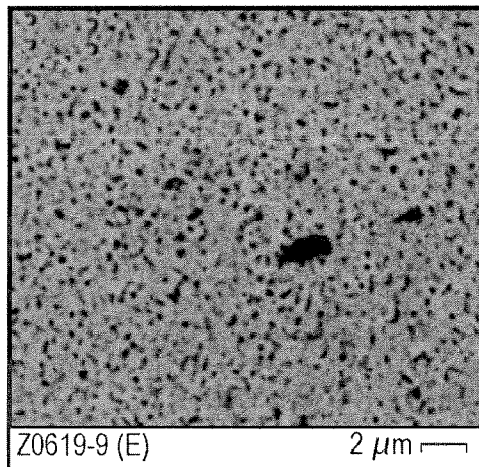


FIG. 17A

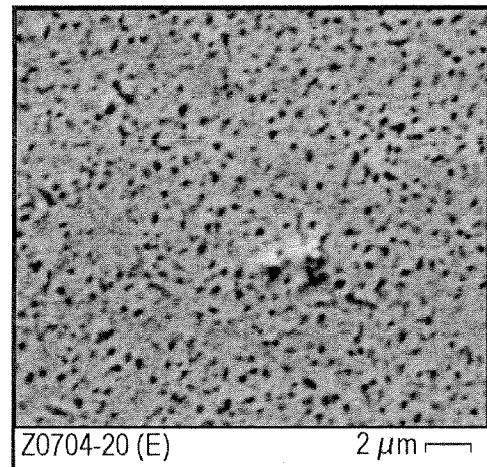


FIG. 17B

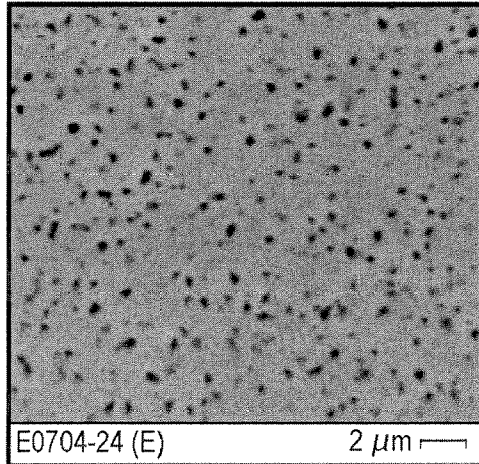


FIG. 17C

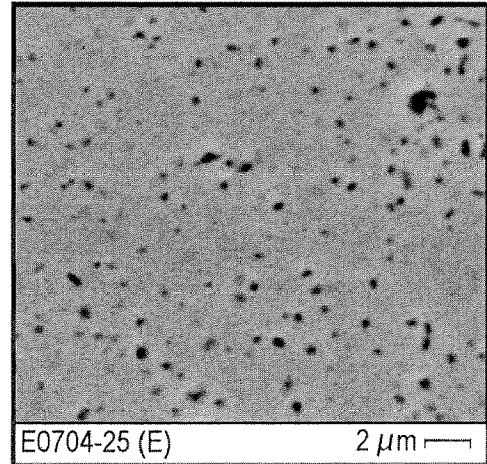


FIG. 17D

19/21

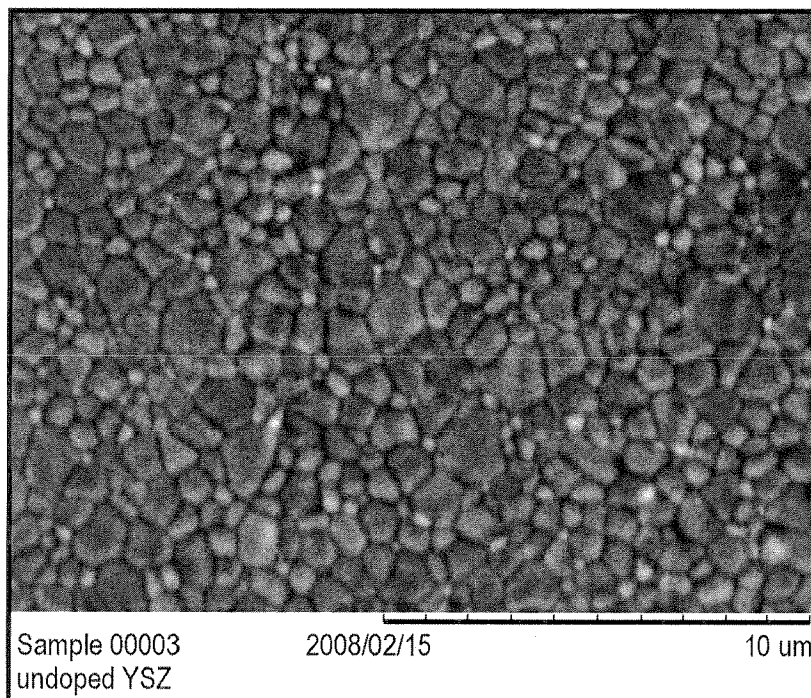


FIG. 18A

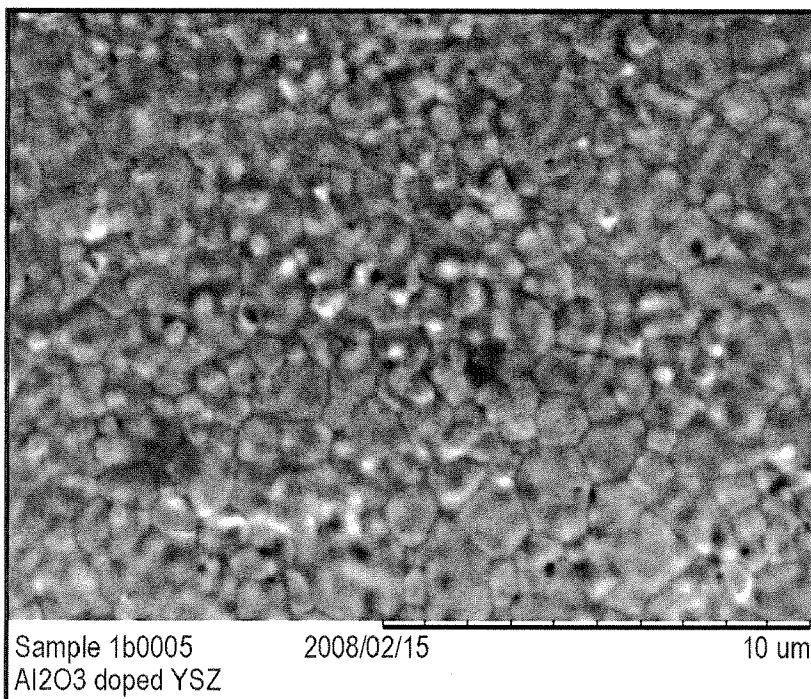


FIG. 18B

20/21

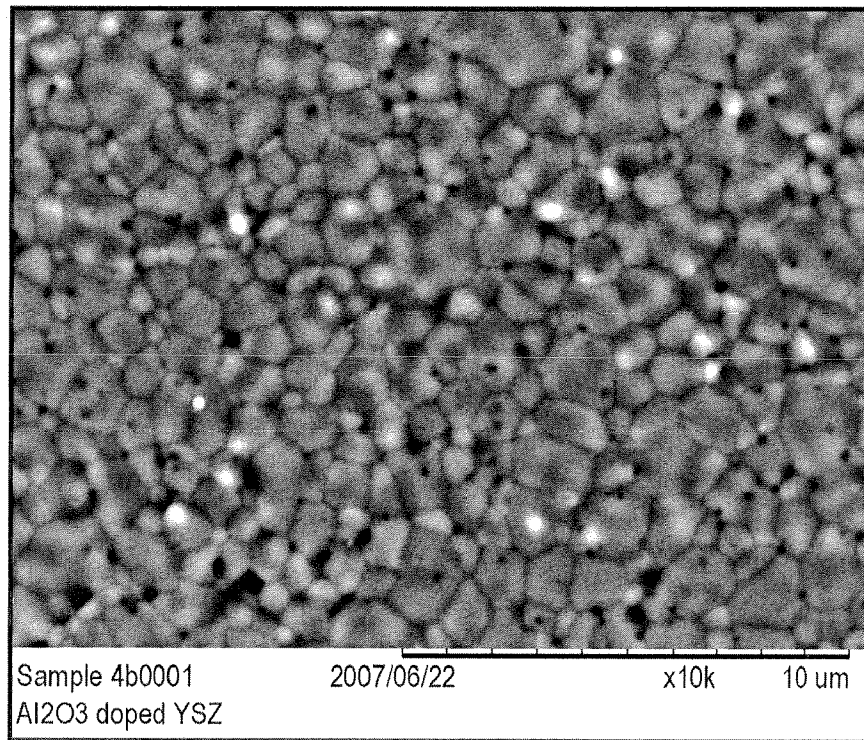


FIG. 18C

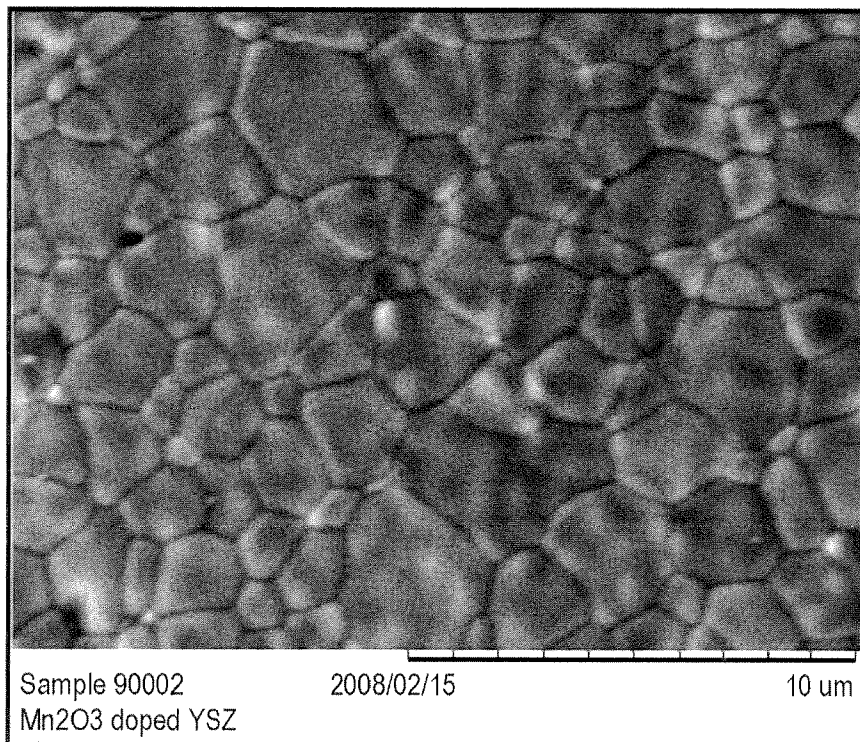


FIG. 18D

21/21

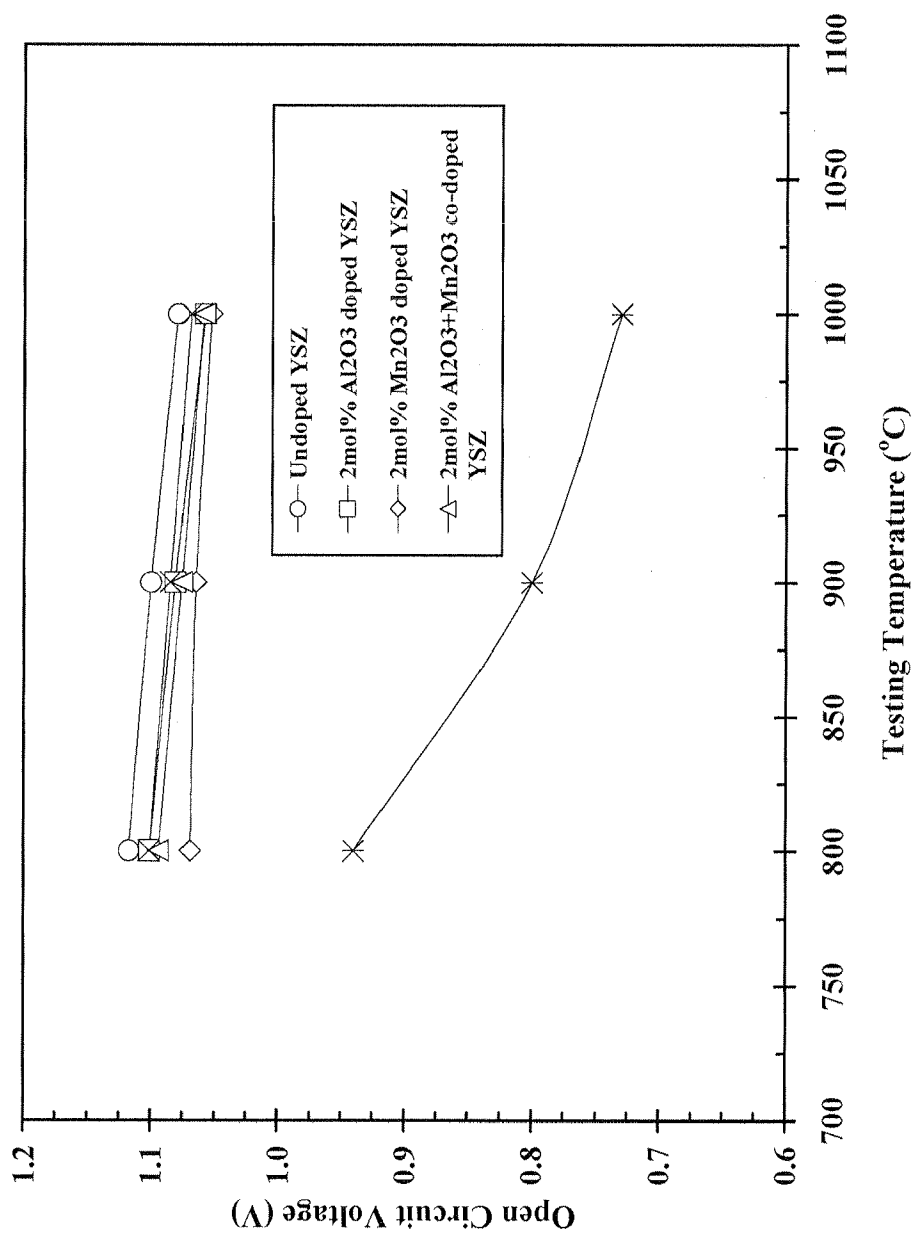


FIG. 19