

# Advances in Solid Oxide Fuel Cells and Electronic Ceramics

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# **Advances in Solid Oxide Fuel Cells and Electronic Ceramics**

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## DURABILITY OF LANTHANUM STRONTIUM COBALT FERRITE ((La<sub>0.60</sub>Sr<sub>0.40</sub>)<sub>0.95</sub>(Co<sub>0.20</sub>Fe<sub>0.80</sub>)O<sub>3-x</sub>). CATHODES IN CO<sub>2</sub> AND H<sub>2</sub>O CONTAINING AIR

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Figure 8. CO<sub>2</sub> production under temperature programmed oxidation (TPO) in 5 %O<sub>2</sub>-He at a heating rate of 10°C/min for Ni-YSZ (solid line) and Ni-ScSZ (dotted line) cermet after exposure to 10 %CH<sub>4</sub>-N<sub>2</sub> for 1 h at 800 and 1000°C. The spectrum for Ni-ScSZ cermet exposed at 1000°C is separated into three curves (C<sub>α</sub>, C<sub>β</sub> and C<sub>γ</sub>).

Figure 9. Raman spectra for Ni-YSZ anode in an electrolyte-supported planar SOFC. Before discharge, the anode was exposed to 10 %CH<sub>4</sub>-N<sub>2</sub> mixture without current loading for 1 h at 1000°C. The discharge condition was at 0.3 A/cm<sup>2</sup> for 1 h in 5 %H<sub>2</sub>O-10 %CH<sub>4</sub>-N<sub>2</sub> at 1000°C. The spectra are normalized to the intensity of G band at 1580 cm<sup>-1</sup> (I<sub>G</sub>).

Figure 10. AC impedance spectra (a, b) between the anode and reference electrode for the electrolyte-supported cells and (c, d) between the anode and cathode for the anode-supported cells in various mixtures at 650 and 800°C.

Figure 11. Raman mapping image for the Ni-YSZ in anode-supported cells after discharge for 20 h (a) at 0.1 A/cm<sup>2</sup> and 650°C in CO<sub>2</sub>-CO mixture and (b) at 0.2 A/cm<sup>2</sup> and 800°C in H<sub>2</sub>O-CH<sub>4</sub> mixture. The stronger the peak intensity is, the darker mapping images become.

Figure 12. Time courses of weight ratio of deposited carbon to catalyst with a supply of 10 %Fuel-3 % H<sub>2</sub>O-N<sub>2</sub> (Fuel: CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>10</sub> and *n*-C<sub>4</sub>H<sub>10</sub>) after reduction for 2 h in 10 %H<sub>2</sub>-3 % H<sub>2</sub>O-N<sub>2</sub> for Ni-GDC at 650°C.

Figure 13. Time courses of weight ratio of deposited carbon to catalystin 11 %*n*-C<sub>4</sub>H<sub>10</sub>-6 %*i*-C<sub>4</sub>H<sub>10</sub>-0 %H<sub>2</sub>O (dry) or 3 %H<sub>2</sub>O (wet)-N<sub>2</sub> after reduction for 1 h with a supply of 57 %H<sub>2</sub>-3 % H<sub>2</sub>O-N<sub>2</sub> for Ni-YSZ, Ni-ScSZ and Ni-GDC at 600°C.

Figure 14. Time courses of cell voltage at 0.2 A /cm<sup>2</sup> for anode-supported microtubular cells with Ni-YSZ, Ni-ScSZ and Ni-GDC anodes at 610, 660 and 710°C in 11 %*n*-C<sub>4</sub>H<sub>10</sub>-6 %*i*-C<sub>4</sub>H<sub>10</sub>-3 %H<sub>2</sub>O-N<sub>2</sub>.

Figure 15. Scanning electron microscope images of (a) Ni-YSZ, (b) Ni-ScSZ and (c-e) Ni-GDC anodes after direct butane utilization at (a-c) 610, (d) 660 and (e) 710°C.

Figure 16. Photos of (a) 36 microtubular cells stack with Ni-GDC anode, and (b) a prototype portable SOFC system using a commercially available LPG cartridge.

Figure 17. Current-voltage and power characteristics of a prototype portable SOFC with 36 microtubular cells stack using hydrogen and LPG fuels at 600 and 650°C.

Figure 18. (a) Schematic framework of NEDO project “Technology Development of Portable Electricity Generator Using Micro SOFC” and (b) Schematic appearance of a 200 W-class portable electricity generator using micro SOFCs.

## HIGHLY EFFICIENT SOLID OXIDE ELECTROLYZER AND SABATIER SYSTEM

**Figure 1. Corning’ s Multi-Strip Cell Electrolyte Supported Fuel Cell**



**Figure 2** Packet Containing Two Multi-strip cells in Electrolyzer mode

**Figure 3.** Illustration of SOE/ESR Stack

**Figure 4** Bare Electrolyte Substrate

**Figure 5** A Close up of the Via Hole in the Substrate

**Figure 6** Multi-strip Cell after Anode Printing

**Figure 7** Completed Multi-Strip Cell

**Figure 8** Dispensing of Glass-Ceramic Frit Paste on the Perimeter of the Substrate

**Figure 9** Finished Assembly without the Tubes

**Figure 10** Finished Two Chamber Assembly with Inlet and Outlet Tubes

**Figure 11** Test Packet Built for Assessing the Seal Integrity

**Figure 12** Initial Thermal Cycle Temperature Profile (Cycles 1-3)

**Figure 13** Additional Thermal Cycle Temperature Profile (Cycles 4-22)

## **THE EFFECTS OF EXCESS SILICON AND CARBON IN SiC SOURCE MATERIALS ON SiC SINGLE CRYSTAL GROWTH IN PHYSICAL VAPOUR TRANSPORT METHOD**

**Figure 1.** One of our recent demonstrations of 150 mm-diameter 4H-SiC single crystal wafers (right), exhibited with 100 mm 4H-SiC wafers for comparison (left).

**Figure 2.** Schematic of a typical growth configuration of PVT method for SiC single crystals. The crucible is heated up to higher temperatures exceeding 2300K with an appropriate temperature

gradient along the longitudinal direction of the crucible, giving rise to thermal decomposition of the source powder whereas in the upper part of the crucible the solidification of SiC from the vapour occurs on the seed crystal.

**Figure 3.** Pressure -dependent phase diagram of Si - C binary system at a fixed temperature of 2500K.

**Figure 4.** Variation of phase diagram as a function of temperature. The figure shows a part of the pressure-dependent Si-C binary phase diagram shown in Figure 3.

**Figure 5.** (a) Schematic of elementary reaction processes responsible for SiC single crystal growth, and (b) corresponding equilibrium phase diagrams of source (solid line) and growing crystal (broken line) inside crucible, respectively.<sup>11</sup>; SiC(s) particles in the source are decomposed by sublimation into graphite C(s) and sublimed vapour ( $v_1$ ) with a composition of  $v_1(g)$ , and the vapour ( $v_1$ ) is transported by diffusion to the seed crystal where the temperature is set to be lower than the source's, followed by the solidification of SiC(s) onto the seed surface with changing the vapour to ( $v_2$ ) of a composition  $v_2(g)$  richer in Si compared to  $v_1(g)$ 's.

**Figure 6.** Graphitization layer formed at the interface between 6H-SiC seed and unintentionally-doped 6H-SiC growing crystal. Fine lines observed in the growing crystal are micropipe defects generated by the interface graphitization layer.

**Figure 7.** (a) Phase diagram at 2500K for Case A, i.e., SiC(s)+C(s) system in which whole source composition is indicated by vertical broken line, and (b) schematic illustrations of equilibrium states

realised in closed cylinder containers under vapour pressures of  $P_I$  and  $P_{II}$ , both indicated in Fig.7(a). The thick black parts placed upper in the cylinder containers correspond to mechanically freely-moveable lids. For more details, see the main text.

**Figure 8.** (a) Si-C phase diagram at 2500K for Case B, i.e.,  $\text{SiC(s)} + \text{Si(s)}$  systems with two whole source compositions indicated by the vertical broken line S1 and S2. Equilibrium states realised at different pressures of  $P_{III}$  and  $P_{IV}$ , for (b) the composition S1 and (c) composition S2 systems, both indicated in Fig.8(a), respectively. Note that (l) in Figure 8(b) and 8(c) represents a Si-C liquid with a composition of  $l_{III}(l)$ . No chemical reactions with cylinder containers are assumed to occur in these systems.

## RECENT PROGRESS OF GaN SUBSTRATES MANUFACTURED BY VAS METHOD

**Figure 1.** Photograph of the self-separated GaN bulk crystal and the base substrate, whose diameters are 116 mm and 125 mm, respectively. On the left is the resulting GaN bulk, and on the right is the base substrate. The graph paper has a 10-mm grid.

**Figure 2.** Photograph of bulk GaN substrate having a 100-mm diameter.

**Figure 3.** Cross-sectional schematic of thick growth on a concave substrate.

**Figure 4.** Normalized growth thickness dependence of the curvature.

**Figure 5.** Photograph of the heavily Si -doped GaN on a bulk GaN substrate.

**Figure 6.** Appearance of the as-grown bulk GaN having the highest carrier concentration and lowest

resistivity in this study.

**Figure 7.** Normalized  $\text{GeCl}_4$  supply dependence of the carrier concentration and resistivity.

**Figure 8.** Spectra of the optical-absorption coefficient for Ge-doped samples for which carrier concentrations are different.

**Figure 9.** Carrier concentration dependence of optical-absorption coefficient at 3.0 eV.

**Figure 10.** Dislocation density of Ge-doped or Si-doped samples as a function of carrier concentration.

**Figure 11.** C-plane curvature of Ge -doped or Si-doped samples as a function of carrier concentration.

**Figure 12.** Normalized growth thickness dependence of dislocation density and curvature.

## COILABLE SINGLE CRYSTAL FIBERS OF DOPED-YAG FOR HIGH POWER APPLICATIONS

**Figure 1.** LHPG method

**Figure 2.** Impact of Diameter Control Feedback System

**Figure 3.** Line scan of Nd Concentration in Nd:YAG Single-Crystal Fiber (wt % vs. position). (a) distribution of neodymium atoms in a YAG fiber 100 mm long and 550  $\mu\text{m}$  in diameter, core is 113  $\mu\text{m}$  (b) distribution of Nd after the third regrowth. The diameter of the Nd-doped core shrunk to about 1/7 of diameter of fiber.

**Figure 4:** (a) XRD Measurements of Sol-Gel YAG Cladding Indicate Single-Phase Cubic-Phase YAG Yb:YAG (b) Fiber 130  $\mu\text{m}$  in Diameter Cladded with 3 Sol-Gel Coatings of Polycrystalline YAG.

**Figure 5.** Undoped cladding around a doped core

**Figure 6.** Nd:YAG Single-Crystal Fiber optical damage experiment

## **HYDROTHERMAL CRYSTAL GROWTH AND APPLICATIONS**

**Figure 1** (a). High pressure security valve system and (b) hydrothermal system interfaced with computer at ICMCB-CNRS

**Figure 2.** Phase diagram of  $\text{SiO}_2\text{-GeO}_2$ .

**Figure 3.** EPMA of the grown SGO single crystals by hydrothermal method.

## **REACTIVE ATMOSPHERES FOR OXIDE CRYSTAL GROWTH**

**Figure 1.** Predominance phase diagrams Fe -  $\text{O}_2$  with Gibbs free energy (left) or oxygen partial pressure (right) as ordinate, total pressure is 1 bar.  $p_{\text{O}_2}$  at the triple points of the wüstite phase  $\text{Fe}_{1-x}\text{O}$  (right, inside dashed circles) is from top to bottom:  $2.5 \times 10^{-6}$  bar,  $7.8 \times 10^{-11}$  bar,  $1 \times 10^{-26}$  bar

**Figure 2.** DTA heating curves of FeO. From top to bottom: 1<sup>st</sup> run in Ar, 7<sup>th</sup> run in Ar, arbitrary run in a reactive atmosphere 85% Ar + 10%  $\text{CO}_2$  + 5% CO

**Figure 3.** Isotherms through the  $\text{SiO}_2\text{-Fe-Fe}_2\text{O}_3$  system below and above the eutectoid wüstite decomposition near 840 K. Labels inside ternary phase fields show  $p_{\text{O}_2}$ . At 1400 two binary phase fields “wüstite + fayalite” or “magnetite + high-tridymite” emerge.

**Figure 4.** Left: The free energy for the formation of  $\text{Fe}_2\text{SiO}_4$  from constituent oxides (top) is very small,

compared to the free formation energy of these constituents from the elements. Right: Predominance phase diagram Fe-Si-O<sub>2</sub> (Fe:Si = 2:1), see also right panel of Figure 1.

**Figure 5.** Vertical isopleth section through the center of the Gibbs triangles in Figure 3, crossing the fayalite (Fe<sub>2</sub>SiO<sub>4</sub>) composition. The red dots (right ordinate) represent the equilibrium oxygen partial pressure along the liquidus.

**Figure 6.** Fugacity of main gaseous species along the liquidus of Fe<sub>2</sub>SiO<sub>4</sub>. Note that the red (O<sub>2</sub>) line corresponds to the dotted red line in Figure 5.

**Figure 7.** Top: DTA/TG measurements (heating/cooling with  $\pm 10$  K/min) of V<sub>2</sub>O<sub>5</sub>/MoO<sub>3</sub> mixtures with 14.2 mol% MoO<sub>3</sub> in air or in 5N Ar, respectively. Bottom: Phase fields of vanadium-molybdenum-oxides with V:Mo in slight excess of the ideal 9:6 ratio for V<sub>9</sub>Mo<sub>6</sub>O<sub>40</sub>. The liquid phase of molten V-Mo-oxides is calculated as ideal mixture. The dashed lines represent the  $p_{O_2}$  of air or of the residual gas impurities in Ar with 99.999% purity, respectively. (Reprinted with permission from Cambridge University Press<sup>18</sup>.)

## DISCUSSION ON POLYCRYSTALS OVER SINGLE CRYSTALS FOR OPTICAL DEVICES

**Figure 1.** Transparent PCA ceramics obtained with different sintering parameters (The encircled are the samples with best transparencies).

**Figure 2.** SEM micrographs of YLO ceramics (a) 1500°C, 100 MPa,  $t_8 = 5$  min and Rh=50°C/min, annealed at 1200°C for 12 h (b) 1700°C, 100 MPa,