

Combustion Synthesis of Si₃N₄ by Selective Reaction of Silicon with Nitrogen in Air

Jiang-Tao Li,[‡] Lin Mei,^{†,‡,§} Yun Yang,^{‡,§} and Zhi-Ming Lin[‡]

[‡]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[§]Graduated School of the Chinese Academy of Sciences, Beijing 100039, China

Silicon nitride (Si₃N₄) was synthesized by a selective combustion reaction of silicon powder with nitrogen in air. The α/β -Si₃N₄ ratio of the interior product could be tailored by adjusting the Si₃N₄-diluent content in the reactant mixtures. The synthetic β -Si₃N₄ showed a well-crystallized rod-like morphology. Mechanical activation greatly enhanced the reactivity of silicon powder, and the slow oxidation of silicon at the sample surface promoted the combustion reaction in air. The formation mechanism of Si₃N₄ was analyzed based on a proposed N₂/O₂ diffusion kinetic model, and the calculated result is in good agreement with the experimental phenomenon.

I. Introduction

 $S_{\rm ILICON}$ nitride $({\rm Si}_3{\rm N}_4)$ is a promising material for high-temperature applications due to its high strength, high toughness, excellent chemical stability, and wear resistance.¹ For the synthesis of Si₃N₄ powder, direct nitridation, carbothermal reduction, vapor-phase reactions, and thermal decomposition are the most commonly used processes.² Combustion synthesis (CS) of Si₃N₄ powder is also an attractive technology because of its greater energy efficiency, higher product purity, and shorter production cycle.³ The theoretically calculated nitrogen pressure required for carrying out the CS of Si₃N₄ is over 10⁴ MPa.⁴ However, the practical nitrogen pressure for CS of Si₃N₄ has been decreased from 100 to 1.2 MPa due to the continuous efforts of many researchers.^{5,6} It is demonstrated that the gas-solid interfacial reaction between nitrogen and silicon can be enhanced effectively by mechanical activation (named hereafter as MA). These results indicate a potential of realizing CS of Si₃N₄ under a much lower nitrogen pressure, which is strongly desirable from the viewpoint of cost and safety.

Recently, the feasibility of synthesizing nitrogen ceramics by combustion of several metallic powders in air has been reported. For example, combustion of ultra-fine Al particle and (Al+C) powders in air led to the formation of Al N instead of Al_2O_3 .^{7,8} The TiN powder could also be synthesized by combustion of Ti powder in air.⁹ These results suggest that single-phase nitrogen ceramics could be synthesized through the selective nitriding combustion of metallic powders with N₂ in air, which provides a possibility of synthesis and sintering of nitrogen ceramics in a conventional kiln furnace without any atmosphere protection.

The present work attempts to synthesize Si_3N_4 powder by combustion of nonmetallic powders containing $Si/Si_3N_4/NH_4Cl$ in air, with the assistance of MA, and attempts to discuss the formation mechanism of Si_3N_4 based on a proposed kinetic model of N_2/O_2 diffusion.

II. Experimental Procedure

All reagents were obtained from the Chinese Chemical Market and used as supplied: Si powder (purity >98.5 wt%, 0.4-0.7 wt% Fe, 45 µm, General Research Institute for Nonferrous Metals, Beijing, China), α -Si₃N₄ (α -ratio >93.0 wt%, 1.5 wt% oxygen, 5.0 µm, Shanghai Junyu Ceramic-Molded Product Co. Ltd., Shanghai, China), and NH₄Cl (purity >99.3 wt%, Analytical Reagent, Beijing Chemical Corporation, Beijing, China) as grinding aids. According to the mass ratio shown in Table I, the reactant powders were dry blended and attrition milled for different duration of time in a sealed agate jar, using ZrO₂ balls as the milling media, with a ball/charge weight ratio of 10:1. The jar was made to vibrate at amplitude A = 3-6 mm and frequency f = 24.3 Hz. Then the as-activated powders were sieved through a 200-mesh screen and loaded loosely into a horizontal quadrate graphite die of 220 mm length, 95 mm width, and 70 mm height, which was placed in air. The sample weight was fixed to 400.0 g and the initial porosity was estimated to be 70%. The combustion reaction was initiated by igniting a titanium powder compact placed on the top of the reactant. A W-Re3/W-Re25 thermocouple was inserted directly into the sample interior to record the temperature history of the combustion reaction.

The phase assemblage of the as-synthesized product was identified by X-ray diffraction (XRD; D/max-RB, Rigaku, Japan) using CuK α radiation ($\lambda = 1.54056$ nm) with a step of 0.02°. The phase content of α/β -Si₃N₄ was determined according to Gazzara's method.¹⁰ The microstructure of the product was examined by scanning electron microscopy (SEM; JSM-6460LV, JEOL, Japan). Fourier-transform infrared spectra (FTIR; Excalibur 3100, Varian, Walnut Creek) were also used to analyze the product, with a resolution of 0.20 cm⁻¹. Further quantitative analysis was carried out by X-ray fluorescence spectroscopy (XRF; XRF-1800, Shimadzu, Kyoto, Japan) using higher-order X-rays, where the percentage contents of Si, N, O, Fe, and C were determined on BG–FP model.

III. Results

In order to identify the feasibility of the combustion reaction of silicon powder in air, six experiments with different milling times were performed, as shown in Table I. Only the reactants milled for 16 h could be initiated to burn and self-propagated to all the samples in the form of a combustion wave. After the combustion reaction was over and the sample was cooled down, products were collected from different locations, viz. the surface (H = 0-7 mm) and the interior (H = 7-35 mm), respectively, as shown in Fig. 1. The whole product existed as a loose compact that could be easily pulverized into powders by hand, while the samples taken from the surface and interior showed different colors.

S. Danforth-contributing editor

Manuscript No. 25181. Received September 2, 2008; approved December 5, 2008. This work was financially supported by National Natural Science Foundation of China (Grant nos. 50502035 and 50772116).

[†]Author to whom correspondence should be addressed. e-mail: meilinipc@gmail.com

Table I. Starting Compositions and Experimental Conditions

	Starting composition	Milling time (h) and reaction characteristic	
Sample	Si:Si ₃ N ₄ :NH ₄ Cl (wt%)		
C1	60.5:25:14.5	$0(N)^{\dagger}, 8(N), 12(N), 16(Y)$	
C2	80.5:5:14.5	16(Y)	
C3	35.5:50:14.5	16(Y)	

 † The abbreviation xx(Y/N) means that the combustion reaction could be realized (Y) or not (N), with the reactants premilled for xx h.

Then the powder products were analyzed by XRD, and the results are presented in Fig. 2. XRD patterns showed that the product at the surface mainly consisted of α -Si₃N₄ and β -Si₃N₄, except for a small amount of Si₂N₂O. However, the loose powder taken from the interior was composed of single-phase Si₃N₄. This is well consistent with the FTIR and XRF analysis results (see Fig. 3). The absorption bands at 1039, 940, 915, 885, 576, and 440 cm⁻¹ were attributed to antisymmetric and symmetric stretching vibrations of the Si-N bond, which further confirmed that the powder collected from the interior was Si₃N₄, with only 4.72 wt% oxygen.¹¹ FTIR analysis also demonstrated that a mass of SiO₂ existed in the surface product, corresponding to the intensive absorption bands at 1094 and 494 cm^{-1,12} Meanwhile, the oxygen content of the surface product increased considerably to 26.8 wt%, although no diffraction peaks of SiO₂ were found in the XRD patterns. This suggests that SiO₂ detected by FTIR and XRF is amorphous, which may be caused by the rapid oxidation-combustion of Si powder on the sample surface. Therefore, Si₃N₄ was the dominant phase in the product block, and its available scope is designated by a dashed circle shown in Fig. 1.

According to Gazzara's method, the products collected from the interior of sample C1 contained 55.21 wt% α -Si₃N₄. For tailoring the α/β -Si₃N₄ ratio of the product, different amounts of Si₃N₄ diluent were introduced into samples C2 and C3, viz. 5 and 50 wt%, respectively. As shown in Figs. 2(c) and (d), the products from sample C2 were β -Si₃N₄, while nearly singlephase α -Si₃N₄ was obtained in sample C3, with only a trace of β -Si₃N₄ and residual Si. This could be attributed to the decrease of combustion temperature from 1983 to 1638 K caused by the massive addition of Si₃N₄ diluent, therefore, the phase transformation from α -Si₃N₄ to β -Si₃N₄ was suppressed.

Figures 4(a)–(d) show the SEM images of the combustion products. Both samples C1 and C2 were composed of well-crystallized rod-like grains, which are the typical morphology of β -Si₃N₄. The amplified observation indicated that the Si₃N₄ rodlike grains in sample C1 were ~0.3 µm in diameter and ~3 µm in length, while those in sample C2 exhibited a larger diameter (~1 µm) and a clearer hexagonal columnar morphology. The combustion temperatures of the samples were considerably higher than both the melting point of Si and the eutectic point of the M–Si–O–N system (M = Fe, C). Therefore, an M–Si– O–N liquid could be formed that is beneficial for the α to β phase transformation and the β -Si₃N₄ grain growth by the VLS (vapor–liquid–solid) mechanism.^{13,14} However, sample C3



Fig. 1. Digital camera photograph of the transverse section of sample C1; *H* represents the distance from the sample surface toward the interior.



Fig. 2. X-ray diffraction patterns of the products from samples: (a) C1 surface, (b) C1 interior, (c) C2 interior, and (d) C3 interior. Indexed according to JCPDS cards: 41-0360 (a-Si₃N₄), 33-1160 (β -Si₃N₄), and 84-1813 (Si₂N₂O).

showed a coarse morphology. Because of the lower combustion temperature, solid silicon powder may be converted into α -Si₃N₄ directly.

IV. Discussion

(1) Effects of MA on the Microstructure of Si Powder

To investigate the MA effect during milling, the reactant mixtures with the composition of C1 were mechanically milled for 0, 8, 12, and 16 h, respectively. XRD analysis of the milled reactants was conducted and is shown in Fig. 5. It was found that no new phases appeared in the reactant powders with an increase of the milling time, while the integrated intensity of the diffraction peaks of Si decreased significantly, which may have been caused by the formation of amorphous and nanocrystalline Si particles. This is consistent with the literature report.¹⁵ The degree of amorphization of silicon (*R*) could be calculated according to the equation

$$R = (1 - I/I_0) \times 100\% \tag{1}$$

where *I* is the intensity of the Si₍₁₁₁₎ plane measured from the reactants milled for different times and I_0 is the intensity measured from the nonmilled (i.e., 0 h) powder mixture. It was found that the degree of amorphization of silicon increased considerably with the milling time, as presented in Table II. When the milling time reached 16 h, 50.63% silicon became amorphous. Two possible amorphization mechanisms, i.e., stress-induced amorphization and crystallite refinement-induced amorphization, have been proposed for the amorphization of Si induced by ball milling.¹⁵ Especially for the introduction of NH₄Cl, the pulverizing efficiency was considerably improved in



Fig. 3. Fourier-transform infrared spectra of the products from sample C1: (a) surface and (b) interior, where the inset shows the element contents measured by X-ray fluorescence spectroscopy (XRF).



Fig.4. Scanning electron microscopic images of the interior products from different samples: (a) $C1 \times 4.0$ K, (b) $C1 \times 20$ K, (c) $C2 \times 20$ K, and (d) $C3 \times 4.0$ K.

the milling process.⁶ Therefore, the MA enhanced the reactivity of Si powder reactants, which promoted the CS of Si_3N_4 in air.

(2) Analysis of the Combustion Temperature Profile

Two contrast experiments were performed to deduce the reaction mechanism, in which the sample C1 mechanically activated for 16 h was ignited in air and 0.1 MPa nitrogen atmosphere, respectively. Interestingly, the reactants placed in air underwent a combustion reaction propagating to the whole sample, whereas the combustion reaction could not be sustained in a pure nitrogen atmosphere. It is believed that the O_2 in air plays a critical role in the full combustion of silicon powder. This is why large amounts of Si₂N₂O and SiO₂ were detected by XRD and FTIR on the surface area of the product. It can be concluded that the highly activated Si powder at the sample surface first undergoes an oxidation reaction, accompanied by a mass of heat release. Once the temperature of the local parts reached the ignition point of the Si-N2 reaction, the fully CS was initiated and propagated through the whole sample. This is in good agreement with the recorded combustion temperature profile shown in



Fig. 5. X-ray diffraction patterns of the reactants milled for different times.

Fig. 6. It is obvious that the burning of Si powder in air occurred via a two-stage self-propagating regime. In the first stage, the temperature increased following a low slope, reaching 1473 K at 2000 s, which can be attributed to the slow oxidation reaction of Si powder.¹⁶ Then the second combustion took place; correspondingly, the temperature increased quickly up to the maximum $T_{\text{max}} = 1898$ K. Therefore, it is concluded that the oxidation of silicon powder at the sample surface induced the subsequent nitridation of Si in the form of a combustion reaction.

(3) Kinetic Analysis of the Si $-N_2$ -Selective Reaction

It is generally regarded that the final products after combustion of Si in air should mainly be oxides instead of nitrides, because O_2 is a much stronger oxidizer than N_2 in a redox reaction. Meanwhile, the decomposition temperature of NH_4Cl is as low as 618 K, and so it is reasonable to neglect the contribution of NH_4Cl to the nitridation of silicon powder due to its decomposition during the slow oxidation process (see Fig. 6). However, the present results indicated that the dominating phase of the inner products was Si_3N_4 , while oxides such as Si_2N_2O and SiO_2 were detected only in the surface products. To explain this phenomenon, a N_2/O_2 diffusion kinetic model is proposed as follows:

Typically, a cylindrical reaction zone with d = 30 mm is chosen for this study. It is assumed that N₂/O₂ should infiltrate continuously from the sample surface to the combustion wave front after the gas–solid combustion reaction is initiated, as shown in Fig. 7. As the pore diameter of the green compacts is much larger than the mean free path of N₂/O₂ molecules, the infiltration of N₂/O₂ in the porous sample can be considered as normal diffusion.¹⁷ Assuming that the infiltration paths are

 Table II.
 Degree of Amorphization of Silicon in the Reactants Milled for Different Duration of Time

Milling time (h)	0	8	12	16	
Integrated diffraction	$42285(I_0)$	20813	15306	12121	
intensity (I)					
Degree of	0	15.78	37.65	50.63	
amorphism (R) (%)					



Fig. 6. Temperature profile for the combustion synthesis of Si_3N_4 from sample C1.

composed of a large amount of cylindrical pores with diameter a, the flux of N_2/O_2 at the infiltration distance H can be expressed as

$$J_{i} = \frac{CSD_{i}}{H} \ln \left[\frac{C - C_{i}(H)}{C - C_{i}(0)} \right]$$

$$\tag{2}$$

where *C* is the concentration of ambient air, $C_i(0)$ is the concentration of N₂ and O₂ at the surface, and $C_i(H)$ is the concentration of N₂ and O₂ at distance *H*. In the present case, $C = 40.88 \text{ mol/m}^3$, $C_N(0) = 31.88 \text{ mol/m}^3$, and $C_O(0) = 8.58 \text{ mol/m}^3$. In particular, both $C_N(H)$ and $C_O(H)$ equal to 0, because the infiltration velocity of N₂/O₂ is much lower than the reaction velocity. *S* is the overall areas of diffusion pores. D_i is the diffusion coefficient as given by¹⁸

$$D_{\rm i} = \frac{2}{3} a \sqrt{\frac{8RT}{\pi M_{\rm i}}} \frac{V_{\rm P}}{\tau} \tag{3}$$

where *R* is the gas constant, *T* is the temperature of the porous sample, M_i is the molecular weight of gas, V_P is the porosity of sample, and τ is the tortuosity factor. As for cylindrical diffusion pores, $\tau = 1$.

In the present case, the measured values are as follows: $T_{\text{max}} = 1898$ K, $V_{\text{P}} = 60\%$, a = 30.0 µm, thus, $T = T_{\text{max}}/2 = 949$ K, $S = 0.25\pi d^2$, and $V_{\text{P}} = 423.9$ mm². According to Eqs. (2) and (3), J_i can be given as

$$J_{N_2} = \frac{2.72 \times 10^{-4}}{H} \tag{4-1}$$

$$J_{O_2} = \frac{3.87 \times 10^{-5}}{H} \tag{4-2}$$

According to Eq. (4), the dependence of J_i on the infiltration distance H was calculated and is shown in Fig. 8. Provided that no reactions occur between N₂/O₂ and Si during the infiltration process, the calculated infiltration flux ratio of N₂/O₂ is 6.99 at



Fig. 7. Illustration of the N_2/O_2 diffusion kinetic mode: (A) longitudinal section, (B) cross section.



Fig. 8. Infiltration flux J_i of N_2/O_2 at different distances *H*.

the interior of the sample, which is far higher than that at the surface (i.e., 31.88/8.58 = 3.72). Therefore, the combustion reaction between Si and N₂ will be the predominant reaction in the interior of the sample. If the final products consist of only Si₃N₄ and SiO₂, the molar ratio of Si₃N₄/SiO₂ should be (6.99/2):(1/1) = 3.49 and, correspondingly, the weight content of SiO₂ should be 10.92 wt%. Actually, O₂ is overwhelmingly consumed at the sample surface because of the lower infiltration velocity; thus, the oxygen content of the final products detected by XRF analysis was well below 10.92 wt%. This result demonstrates that the kinetic discrepancy of N₂/O₂ diffusion enhanced the selective nitridation reaction of Si in the interior of the sample.

Furthermore, in order to confirm the influence of N_2/O_2 diffusion on the phase stability of the products, two equilibrium reactions in the Si–N–O system in the measured temperature range are considered

$$4Si_3N_4(s) + 3O_2(g) = 6Si_2N_2O(s) + 2N_2(g)$$
(5)

$$2Si_2N_2O(s) + 3O_2(g) = 4SiO_2(s) + 2N_2(g)$$
(6)

The Gibbs-free energy changes of reactions (5) and (6) under the partial pressure of N_2/O_2 , i.e., *P* (N_2) and *P* (O_2), can be expressed as

$$\Delta G_1(P,T) = -249\,000 - [1014 - 16.629 \ln P(N_2) + 24.942 \ln P(O_2)]T$$
(7)

$$\Delta G_2(P,T) = -2284\,936 + [422 + 16.629 \ln P(N_2) - 24.942 \ln P(O_2)]T$$
(8)



Fig.9. Phase stability diagram as a function of the partial pressure of nitrogen and oxygen at T = 1898 K.

In an equilibrium state,

$$\Delta G(P,T) = 0 \tag{9}$$

According to Eqs. (7)–(9), the phase stability diagram is constructed at T = 1898 K, which is the maximum measured value during the combustion reaction in air. Thus, the phase stability diagrams are constructed as a function of nitrogen and oxygen partial pressures, as shown in Fig. 9. The value of the $\ln P(O_2)$ is -1.56 in air (marked as area A), which leads to the formation of Si₂O₂N and SiO₂ in the surface products. As shown in Fig. 8, the infiltration flux of N₂/O₂ decreased remarkably with an increase in the diffusion distance. Because of the consumption at the sample surface, the partial pressure of O₂ decreased quickly to a much lower value than that of N₂ (marked as area B). Therefore, the synthesis of single-phase Si₃N₄ in the sample interior is quite favorable.

V. Conclusions

Nitriding CS of Si₃N₄ in air was realized through the selective reaction of Si with N₂. The α/β -Si₃N₄ ratio of the interior products could be easily tailored by adjusting the Si₃N₄-diluent content in the reactant mixtures, and nearly single-phase α -Si₃N₄ and β -Si₃N₄ powders were synthesized at the Si₃N₄-diluent contents of 50 and 5 wt%, respectively. The as-synthesized β -Si₃N₄ showed a well-crystallized rod-like morphology.

The reactivity of Si powder was enhanced remarkably by MA treatment. The surface Si powder exposed to air was prone to oxidation with a mass of heat release, which mainly contributed to the subsequent nitridation of Si powder in air. The discrepancy in the penetrability of N_2/O_2 in the porous media is responsible for the different phase assemblages formed at different regions along the gas infiltration direction. Based on the proposed N_2/O_2 to the sample interior is 6.99, which is responsible for the sample interior of Si powder with nitrogen in the interior of the samples.

References

¹F. L. Riley, "Silicon Nitride and Related Materials," J. Am. Ceram. Soc., 83 [2] 245–65 (2000).

²H. Lange, G. Wotting, and G. Winter, "Silicon Nitride from Powder Synthesis to Ceramic Material," *Ang. Chem. Int. Ed. Engl.*, **30**, 1579–97 (1991).

³K. Hirao, Y. Miyamoto, and M. Koizumi, "Synthesis of Silicon Nitride by a Combustion Reaction Under High Nitrogen Pressure," *J. Am. Ceram. Soc.*, **64**[7] C-60–1 (1986).

4Z. A. Munir and J. B. Holt, "The Combustion Synthesis of Refractory Nitrides – Part I: Theoretical Analysis," *J. Mater. Sci.*, 22, 710–4 (1987).

 $^5 I.$ G. Cano and M. A. Rodriguez, "Synthesis of $\beta\text{-}Si_3N_4$ by SHS: Fiber Growth," Scr. Mater., **50**, 383–6 (2004).

⁶H. B. Jin, Y. Yang, Y. X. Chen, Z. M. Lin, and J. T. Li, "Mechanochemical– Activation–Assisted Combustion Synthesis of α-Si₃N₄," *J. Am. Ceram. Soc.*, **89** [3] 1099–102 (2006).

⁷A. Gromov and V. Vereshchagin, "Study of Aluminum Nitride Formation by Superfine Aluminum Powder Combustion in Air," *J. Eur. Ceram. Soc.*, **24**, 2879–84 (2004).

⁸T. Tsuchida and T. Hasegawa, "TG–DTA–MS Study of Self-Ignition in Self-Propagating High-Temperature Synthesis of Mechanically Activated Al–C Powder Mixture," *Thermochim. Acta*, **276**, 123–9 (1996).

⁹G. H. Liu, K. X. Chen, H. P. Zhou, K. G. Ren, and H. B. Jin, "Dynamically Controlled Formation of TiN by Combustion of Ti in Air," *J. Am. Ceram. Soc.*, **90** [9] 2918–25 (2007). ¹⁰P. C. Gazzara and D. R. Messier, "Determination of Phase Content of Si₃N₄

¹⁰P. C. Gazzara and D. R. Messier, "Determination of Phase Content of Si₃N₄ by X-Ray Diffraction Analysis," *Am. Ceram. Bull.*, **56**, 777–80 (1977).

 $^{11}T.$ Jie, M. Ye, Y. C. Wu, and L. D. Zhang, "Fourier Transform Infrared Spectroscopy and Raman Spectrum Analyses of Monocrystalline α -Si₃N₄ Nanowires," *J. Chin. Ceram. Soc.*, **36** [1] 44–8 (2008).

¹²J. M. Qian, J. P. Wang, G. J. Qiao, and Z. H. Jin, "Preparation of Porous SiC Ceramic with a Woodlike Microstructure by Sol-Gel and Carbothermal Reduction Processing," *J. Eur. Ceram. Soc.*, **24**, 3251–9 (2004).
¹³W. K. Li, D. Y. Chen, B. L. Zhang, H. R. Zhuang, and W. L. Li, "Effect of

¹³W. K. Li, D. Y. Chen, B. L. Zhang, H. R. Zhuang, and W. L. Li, "Effect of Rare-Earth Oxide Additives on the Morphology of Combustion Synthesized Rod-Like β-Si₃N₄ Crystals," *Mater. Lett.*, **58**, 2322–5 (2004).

Iteke β-Si₃N₄ Crystals," *Mater. Lett.*, **58**, 2322–5 (2004).
 I⁴D. Y. Chen, B. L. Zhang, H. R. Zhuang, and W. L. Li, "Combustion Synthesis of Network Silicon Nitride Porous Ceramics," *Ceram. Int.*, **29**, 363–4 (2003).
 I⁵T. D. Shen, C. C. Koch, T. L. Mclormick, R. L. Nemanich, J. Y. Huang, and

J. G. Huang, "The Structure and Property Characteristics of Amorphous/Nanocrystalline Silicon Produced by Ball Milling," *J. Mater. Res.*, **10**[1] 139–48 (1995). ¹⁶T. Tsuchida, T. Hasegawa, T. Kitagawa, and M. Inagaki, "Aluminum Nitride

¹⁶T. Tsuchida, T. Hasegawa, T. Kitagawa, and M. Inagaki, "Aluminum Nitride Synthesis in Air from Aluminum and Graphite Mixtures Mechanically Activated," *Leur. Comm. Soc.* **17**, 1703 5 (2004).

J. Eur. Ceram. Soc., 17, 1793–5 (2004).
 ¹⁷F. Xia, X. L. Qian, X. Yang, G. K. Liu, and X. Q. Sun, "Model on Gas Diffusion in Porous Electrode in ZrO₂ Oxygen Sensor," J. Sens. Technol., 2, 123–8 (2001).
 ¹⁸F. Zhao, T. J. Armstrong, and A. V. Virkar, "Measurement of O₂–N₂ Effec-

¹⁶F. Zhao, T. J. Armstrong, and A. V. Virkar, "Measurement of O_2 -N₂ Effective Diffusivity in Porous Media at High Temperatures Using an Electrochemical Cell," *J. Electrochem. Soc.*, **150** [3] A 249–56 (2003).