Microfibrous Entrapped Ni/Al_2O_3 Using SS-316 Fibers for H_2 Production from NH_3

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Using a high-speed and low-cost papermaking technology combined with subsequent sintering process, sinter-locked three-dimensional microfibrous networks consisting of ~2 vol % of 6-μm-diameter SS-316 microfibers were utilized to entrap ~25 vol % of 100–200-μm-diameter porous Al_2O_3 support particulates. Nickel, a most active component for ammonia decomposition, was then dispersed onto the pore surface of the entrapped Al_2O_3 support particulates by incipient wetness impregnation method. The resulting microfibrous catalysts took advantage of large void volume, entirely open structure, high heat/mass transfer, good thermal stability, and unique form factors, thereby leading to good activity for ammonia decomposition and significant reduction of overall bed weight and volume. This composite bed reactor was capable of producing 215 sccm hydrogen over per cm^3 bed volume with ammonia conversion of 99.5% at 650°C. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 1845–1849, 2007
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Introduction

Concerns about fuel processing powered fuel cells for portable/micro electronic devices and passenger propulsion have provided particular impetus for research and development on miniature hydrogen generator.[1–8] Ammonia decomposition allows a single feed stream, simplicity of start-up, and low overall device weight and volume,[4–8] thus making it particularly preferred as an attractive source of hydrogen to power fuel cells for micro/portable power applications. Moreover, the widely used Ni/Al_2O_3 catalysts are most active for this hydrogen production process.[5–7] However, the traditional fixed-bed microreactors packed with catalyst particulates normally suffer from poor intraparticle mass/heat transfer, low contacting efficiency, high pressure drop, mechanical attrition, and catalyst clumping in a way that leads to fluid bypassing.[2–4] Although the microchannel technologies combined with the catalyst washcoats can be used to avoid one or more of the frustrated problems encountered in the packed beds, the surface areas per unit reactor volume remains unacceptably low,[2–4,9,10] thereby leading to low reactor bed utilization efficiency and large reactor weight/volume. Hence, it is important to render novel microstructured materials for developing miniature hydrogen generator in micro/portable fuel cell power system applications. A monolithic anodized aluminum microreactor, with an increase in surface areas, has been developed for ammonia decomposition.[4] Regardless of the use of expensive Ru for achieving good performance, fatal disadvantage of this reactor stems from the low melting point (661°C) of the aluminum body. Kenis and coworkers[8] recently reported a more interesting solution of a microreactor composed of inverted beaded silicon carbide monolith with interconnected micronic pores (0.75–7.5 μm) as supports and Ru as catalysts to enable ammonia decomposition up to 1000°C.

A new class of composite materials made by wet lay papermaking/sintering process can incorporate particles as small as 10 μm into a micrometal fiber matrix.[7,11–14] This approach permits high efficiency microprocess and advanced design of microreactor with many beneficial properties that would solve the frustrated problems encountered in conventional approaches, e.g. traditional packed beds. Our previous micro-

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fibrous composite reactors with entrapment of preferential oxidation CO catalyst particulates and with entrapment of H_2S sorbent particulates for hydrogen fuel cleanup in proton exchange membrane fuel cell applications do both provide threefold or more promotion of bed utilization efficiency, while leading to significant reduction of overall reaction bed weight and volume compared to the packed beds with 1 mm diameter catalyst/sorbent pellets.[13,14] Recently, a microfibrous structure with Ni/CeO_2-Al_2O_3 particles using 8-μm-diameter nickel fibers has been reported and examined with the use for ammonia decomposition, which showed fourfold reduction of the overall bed weight and volume compared to the packed bed with 2-mm catalyst pellets.[7] However, nickel fibers are costly and show tendency to nitrify in ammonia at high temperature (>600°C) that deteriorates the strength of microfibrous structure, which makes corrosion resistant stainless steel fibers an attractive alternative. Herein, as a demonstrated example of this novel approach, sinter-locked microfibrous carriers consisting of ~2.0 vol % of 6-μm-diameter stainless steel fibers were utilized to entrap 100–200-μm-diameter Ni/Al_2O_3 catalyst particulates for CO-free hydrogen production via ammonia decomposition with potential for portable fuel cell power supplies.

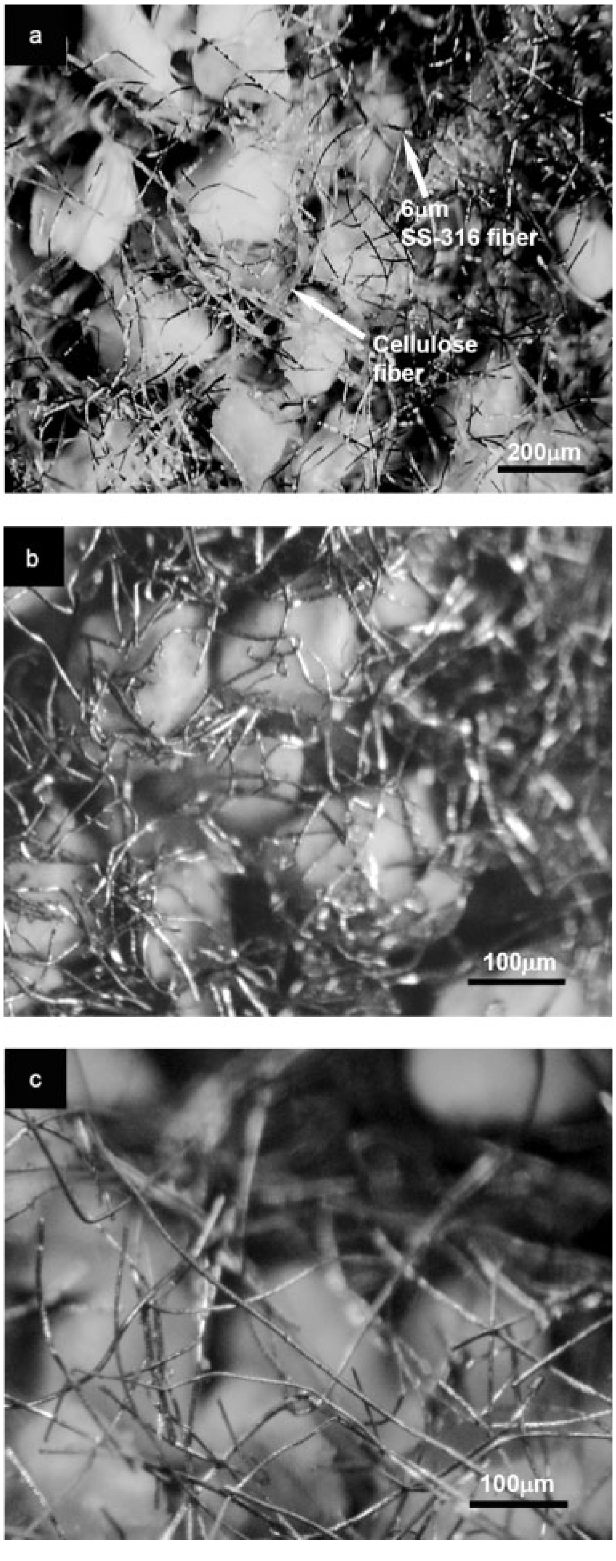

Figure 1. Optical photographs of typical microfibrous structures prepared using 6-μm-diameter SS-316 fibers with 100–200-μm particulates.

(a) Preform paper. (b) Sample *a* after sintering in H_2 at 1000°C for 45 min. (c) Sample *b* after loading nickel through incipient wetness impregnation method. Semitransparent fibers in sample *a* are cellulosic binders. Particulates are active Al_2O_3 supports in samples *a* and *b* and 10 wt % Ni/Al_2O_3 catalysts in *c*.

Experimental

Sintered microfibrous entrapped 100–200-μm-diameter active Al_2O_3 support particulates (initial SA: 270 m^2/g) using stainless steel 316 (SS-316) microfibers (6 μm in diameter by 2–3 mm length; manufactured by Western Metal Material Co., Xian, Shanxi Province, China) was prepared through wet layup papermaking, followed by sintering in hydrogen atmosphere. In this process, 0.7 g of cellulose (20–40 μm diameter by 100–1000 μm length) and 3.0 g SS-316 fibers were added into the container of a commercial blender filled with 1.5 L water and blended vigorously to produce a uniform suspension. The suspension and 5.0 g Al_2O_3 support particulates were transferred into the headbox of a 159-mm-diameter circular sheet former (ZCX-159A, made in China) filled with 8.5 L water under manual mixing. The resulting mixture was then casted into a preform sheet using a wet layup process and dried to create a paper. Preoxidation of the preform paper in air at 500°C removed the cellulosic binders and subsequently sintering in hydrogen at 1000°C for 45 min entrapped the support particulates. Nickel was then highly dispersed onto these entrapped supports by incipient wetness impregnation with nickel nitrate aqueous solution. The nickel loading of 10 wt % was preferable and the optimal catalyst activation temperature was 250°C in air.[7] Catalyst reactivity was measured in a 11.9 mm (i.d.) quartz tube heated by a temperature-controlled tube furnace. Three or five microfibrous discs of 12 mm (diameter) by 0.9 mm (thick) were cut from a large piece of microfibrous catalyst and laid carefully into the tubular quartz reactor. Slightly larger diameter of the catalyst disc than that of the tubular reactor was used to prevent the possibility of a gap between reactor wall and edge

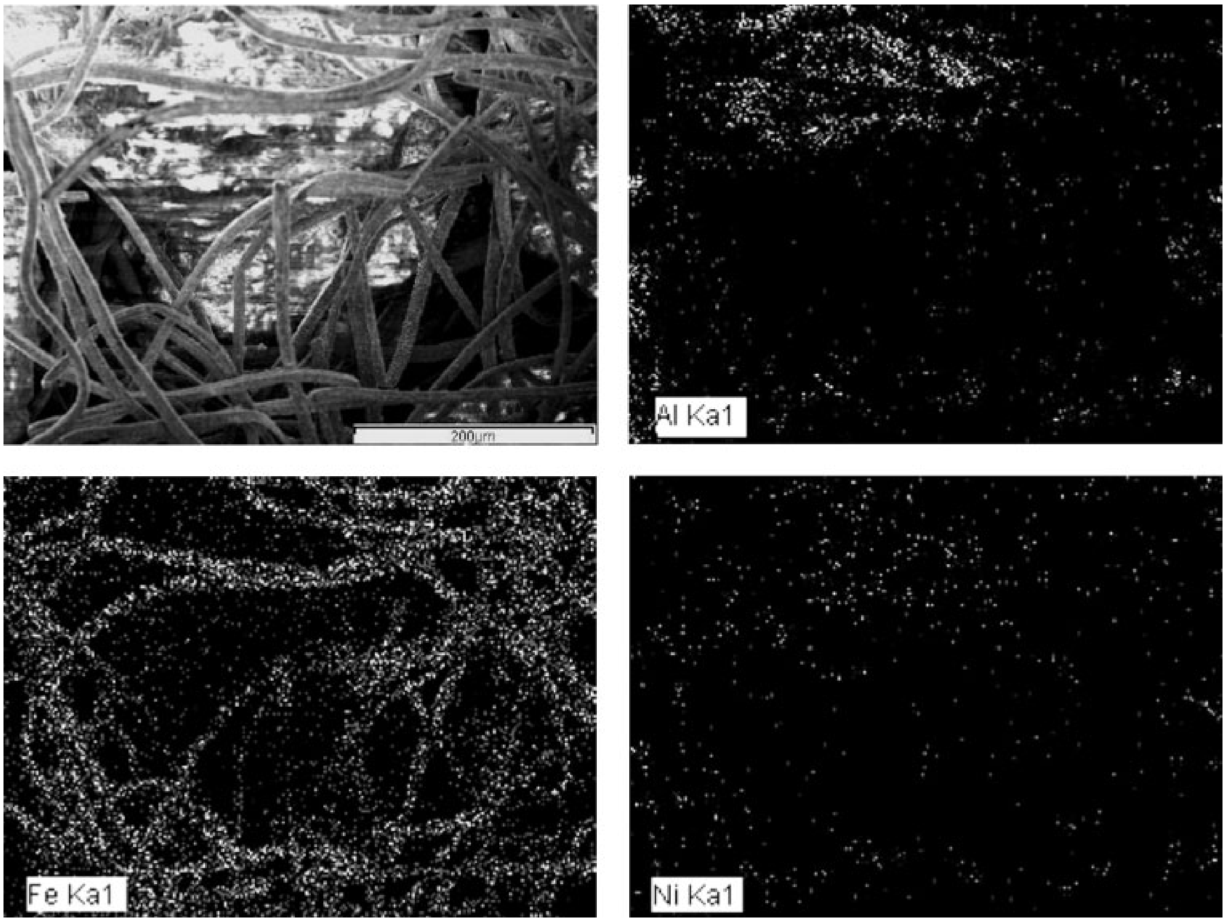

Figure 2. EDX elemental mapping images of Al (from Al_2O_3 particulate), Fe (from SS-316), and Ni for sintered SS-316 fiber entrapped 10 wt % Ni/Al_2O_3.

Photo image (top left); AI mapping image (top right); Fe mapping image (bottom left); Ni mapping image (bottom right).

of catalyst disc, thereby avoiding the gas bypass. Prior to the reaction, catalysts were reduced with H_2 at 500°C for 2 h. Product N_2 and unreacted NH_3 in effluent gas was analyzed at room temperature by an online gas chromatograph equipped with a thermal conductive detector and a 3-m Poropack Q packed column using H_2 carrier gas. NH_3 fractional conversion was calculated by normalization method on nitrogen atom basis.

Photographs of microfibrous structure were recorded by an Olympus zoom stereomicroscope (SZ61). The surface area was determined using Brunauer–Emmet–Teller (BET) method with a commercial unit (Quantachrome Autosorb 3B), with nitrogen physisorption at its boiling temperature. An energy dispersive X-ray (EDX) analyses unit (Oxford, UK) was used for elemental mapping measurements.

Results and Discussion

Microstructure and unique form factor of microfibrous catalyst composite

Figure 1 shows the photographs for the typical microstructure of the microfibrous media with micronic particulates using SS-316 microfibers. Figure 1a shows the pressed and dried paper preform before sintering. A three-dimensional open porous structure of SS-316 microfibers was trussed up with cellulose fibers as binders while locating the micronic Al_2O_3 support particulates into the void space. Figures 1b, c show the sintered products of microfibrous structure with Al_2O_3 support particulates and Ni/Al_2O_3 catalyst particulates, respectively. Clearly, cellulosic binders observed in Figure 1a were completely removed by preoxidation prior to sintering, since no carbon fiber with diameter similar to that of cellulose fibers could be observed in Figures 1b, c. The junctures of metal fibers were well sintered together to form a locked three-dimensional network, thereby uniformly entrapping micronic particulates that were present in the paper (Figures 1b, c). EDX elemental mapping images of Fe, Al, and Ni for the micorfibrous entrapped Ni/Al_2O_3 composite (same sample as in Figure 1c) clearly show that no observable coats of NiO appeared on both fibers and external surface of porous support particulates, suggesting that the nickel species were mostly dispersed onto the internal surface of the porous Al_2O_3 support particulates (Figure 2).

Such microfibrous composite, with unique form factors, can be made into thin sheets (from submillimeter to several millimeters in thickness) of large area and/or pleated sheet

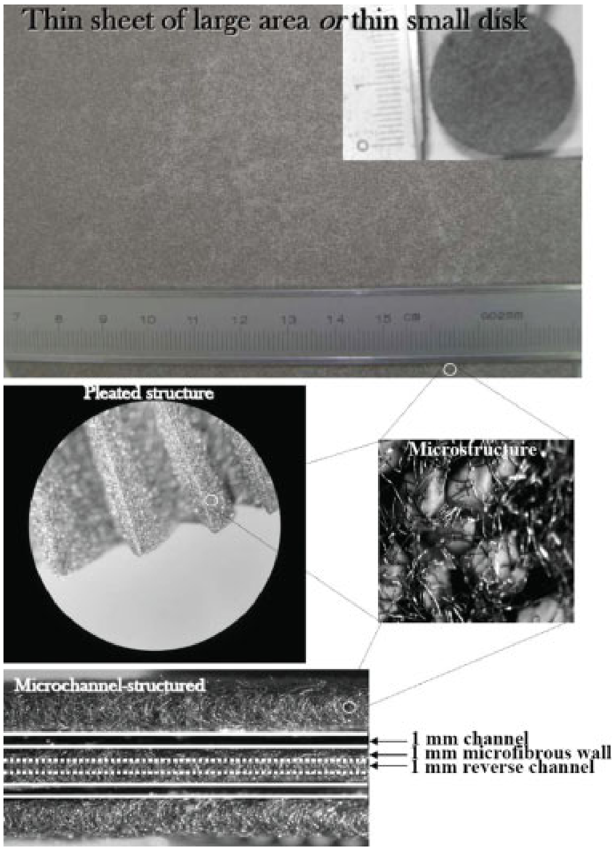

Figure 3. Unique form factors of the microfibrous media with micron-sized particulates using 6-μm-diameter SS-316 fibers.

structure to control pressure drop and contacting efficiency in a beneficial manner different from other traditionally employed contacting schemes including packed beds, fluid beds, honeycombs, or wovens (Figure 3). Note that a new type of microchannel configuration might be derived from such thin-sheet microfibrous composite by carefully pleating it to create unique channel array with desired channel width and depth at its two sides. This design permits fluid to flow along the channel with low pressure drop. Unlike traditional microchannel reactor, pleated sheet structure makes the channel parameters tuning easier and avoids the fin strut that leads to the increase of overall bed volume and weight.

Characteristics of microfibrous composite bed

Table 1 summarizes the characteristics of the microfibrous composite bed and the comparison with a packed bed. The sinter-locked microfibrous network consisting of 2 vol % of 6-μm-diameter SS-316 microfibers offered a very large capacity to load $\sim$25 vol % ($\sim$54 wt %) of the micronic particulates. This new approach increased the catalyst loading by a factor of 3 or much more on a gravimetric basis and by a factor of 1000 on a volumetric basis, compared to traditional microchannel and honeycomb monolith with the washcoats no more than a few microns thick.[10] The microfibrous bed reactors provided larger void volume ($\sim$72 vol %) than the packed bed with 2-mm-diameter pellets ($\sim$30 vol %), and provided much higher surface-to-volume ratio compared to the traditional microchannel and honeycomb monolith (generally less than 10 m^2/cm^3 (Ref. 4)). The microfibrous catalyst composite here gave a surface area of 50 m^2/g, equivalent to a surface-to-volume ratio of 25 m^2/cm^3.

In fact, large void volume and high surface-to-volume ratio as well as the open structure of the microfibrous network are central to the notion of increasing the steady-state volumetric reaction rate. Intraparticle transport can be increased by decreasing the size of the individual particles entrapped in the voids of the microfibrous network, while intrabed transport can be increased by the ability of the microfibrous network to separate particles in the absence of particle–particle contact or the use of traditional binders.[11] Not surprisingly, the microfibrous composite bed exhibited much higher activity for ammonia decomposition while achieving high bed utilization efficiency. At a 90% conversion of a 36 standard cm^3 per min (sccm) ammonia feed rate, the microfibrous composite bed provided a onefold reduction of catalytic bed volume and a 2.8-fold reduction of catalyst weight while leading to a reduction of reaction temperature by 50°C, compared to the packed bed of 2-mm-diameter Ni/Al_2O_3 catalyst (Table 1). Hydrogen production rate of 215 sccm H_2/cm^3 monolith was obtained with an ammonia conversion of 99.5% at 650°C (Table 1), corresponding to an equivalent output power of $\sim$20 W per cm^3 monolith (according to 10.4 sccm H_2 at least per Watt[15]) for a fuel cell.

Figure 4 shows ammonia conversion of various feed rates to 0.5 cm^3 SS-316 microfibrous entrapped 10 wt % Ni/Al_2O_3 composite bed at various temperatures. As we can see, the use of SS-316 microfibrous structure with higher melting temperature permits high temperature operation, thereby being able to yield faster rates or approaching complete ammonia conversion. Nevertheless, higher ammonia conversions (e.g., >95%) could also be achievable at relatively low temperature at the expense of faster rates.

Table 1. Characteristics of Catalytic Beds and Their Reactivity for NH_3 Decomposition*

Catalytic Reaction Bed	Composite Bed	Packed Bed
Nickel loading of Ni/Al_2O_3,[†] wt %	10	10
Fiber, vol %/wt %	2.3/45.5	0
Catalyst particle size, μm	100–200	2000
Catalyst loading, vol %/wt %	25.2/53.5	70.0/100
Void volume fraction,[‡] %	72.5	30.0
Apparent density, g/cm^3	0.45	0.90
Surface-to-volume ratio, m^2/cm^3	25	130
Features for 90% conversion of NH_3 at 36 sccm NH_3 feed		
Volume, cm^3	0.3	0.6
Weight, g	0.14	0.54
Temperature, °C	600	650
Performance of a 72 sccm NH_3 feed at 650°C in 0.5 cm^3 reaction bed		
NH_3 conversion, mol %	99.5	77.0
H_2 production rate, sccm H_2/cm^3 monolith	215.0	166.4

*Each reaction condition was run for 2 h, during which the experimental data were collected.

[†] The values are the nickel content in supported catalyst particulates, not including the mass of fibers.

[‡] Void volume fraction [1 – (volume of fibers + volume of particulates)/total volume of microfibrous media with particulates] × 100.

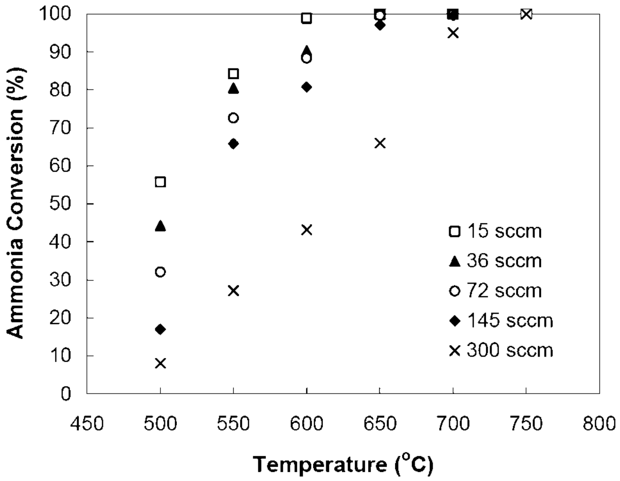

Figure 4. NH_3 conversion versus reaction temperature over 0.5 cm^3 sintered SS-316 fiber entrapped 10 wt % Ni/Al_2O_3 at various feed rates.

Conclusion

The present results established that the microfibrous nickel-based catalyst media were effective for high efficiency production of hydrogen via ammonia decomposition while achieving significant reduction of the overall catalytic bed weight and volume. This approach permitted ~20 W power output hydrogen production rate (i.e., 215 sccm H_2/cm^3 monolith) via ammonia decomposition with a conversion of 99.5% at 650°C. Moreover, the use of SS-316 microfibers as construction material permits operation at higher temperatures for yielding faster rates or approaching complete ammonia conversion. Of course, the commercialization of this small hydrogen generator for miniature fuel cell power system is particularly challenging, as a reactor operating in the real world requires a compact heating source and must meet other performance and reliability criteria.[4,8] However, we anticipate our assay to be a new point for the small-scale production of hydrogen. On the basis of the unique form factors of our micorfibrous composite with enhanced heat/mass transfer, a small plate-type reactor with integrated microcombustor/micro-heater design is considered. The work along this line is in progress in our group.

Acknowledgments

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Literature Cited

1. Neale R. Motorola move communications towards the miniature fuel cell. *Electronic Eng.* 2000;72:9–12.
2. Holladay JD, Wang Y, Jones E. Review of developments in portable hydrogen production using microreactor technology. *Chem Rev.* 2004; 104:4767–4790.
3. Ganley JC, Seebauer EG, Masel RI. Porous anodic alumina microreactors for production of hydrogen from ammonia. *AIChE J.* 2004; 50:829–834.
4. Ganley JC, Seebauer EG, Masel RI. Development of a microreactor for the production of hydrogen from ammonia. *J Power Sour.* 2004; 137:53–61.
5. Chellappa AS, Fischer CM, Thomson WJ. Ammonia decomposition kinetics over Ni-Pt/Al_2O_3 for PEM fuel cell applications. *Appl Catal A: Gen.* 2002;227:231–240.
6. Hacker V, Kordesch K. Ammonia cracker. In: Vielstich W, Lamm A, Gasteiger H, editors. *Handbook of Fuel Cells—Fundamentals, Technology and Applications*, Vol. 3. Chichester: Wiley, 2003: Chapter 10.
7. Lu Y, Wang H, Liu Y, Xue QS, Chen L, He MH. Novel microfibrous composite bed reactor: high efficiency H_2 production from NH_3 with potential for portable fuel cell power supplies. *Lab Chip.* 2007;7:133–140.
8. Christian, Mitchell M, Kim D-P, Kenis PJA. Ceramic microreactors for on-site hydrogen production. *J Catal.* 2006;241:235–242.
9. Watanabe K, Sakairi M, Takahashi H, Takahiro K, Nagata S, Hirai S. Anodizing of aluminum coated with silicon oxide by a sol-gel method. *J Electrochem Soc.* 2001;148:B473–B481.
10. Wu X, Weng D, Xu L, Li H. Structure and performance of gamma-alumina washcoat deposited by plasma spraying. *Surf Coat Technol.* 2001;145:226–232.
11. Harris DK, Cahela DR, Tatarchuk BJ. Wet layup and sintering of metal-containing microfibrous composites for chemical processing opportunities. *Compos A: Appl Sci Manuf.* 2001;32:1117–1126.
12. Cahela DR, Tatarchuk BJ. Permeability of sintered microfibrous composites for heterogeneous catalysis and other chemical processing opportunities. *Catal Today.* 2001;69:33–39.
13. Chang BK, Lu Y, Tatarchuk BJ. Microfibrous entrapment of small catalyst or sorbent particulates for high contacting-efficiency removal of trace contaminants including CO and H_2S from particle reformates for PEM H_2-O_2 fuel cells. *Chem Eng J.* 2006;115:195–202.
14. Lu Y, Sathitsukasnoh N, Queen A, Tatarchuk BJ. Microfibrous entrapped ZnO/support sorbents for high contacting efficiency H_2S removal from reformate streams in PEMFC applications. In: Wang Y, Holladay JD, editors. *Microreactor Technology and Process Intensification.* New York, NY: American Chemical Society Publications Division, Distributed by Oxford University Press, 2005: Chapter 25.
15. Hung Y, Tawfik H. Testing and evaluation of aluminum coated bipolar plates of PEM fuel cells operating at 70°C. In: *Proceedings of FUELCELL2005.* Third International Conference on Fuel Cell Science, Engineering and Technology, Michigan, May 23–25, 2005: FUELCELL-74018.

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