Porous Anodic Alumina Microreactors for Production of Hydrogen from Ammonia

Jason C. Ganley, E. G. Seebauer, and Richard I. Masel
Dept. of Chemical Engineering, University of Illinois, Urbana, IL 61801

DOI 10.1002/aic.10078

The synthesis and properties are described of a ruthenium-impregnated anodic aluminum catalyst for use in microreactors for the production of hydrogen from an ammonia feed. The catalyst structure was synthesized using microelectric discharge machining to create a series of 300 × 300-μm posts on an aluminum substrate. The posts were anodized to yield a 60-μm covering of anodic alumina, with an average surface area of 16 m^2/gm and an average pore size of 50 nm. Ruthenium metal was dispersed on the alumina using conventional wet impregnation. A 0.9 × 0.9-cm reactor containing 250 posts decomposed 95% of anhydrous ammonia at 650°C to yield 15 sccm of hydrogen. A possible application of these microreactor fabrication methods is hydrogen generation for fuel cells in mobile power production. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 829–834, 2004
Keywords: ammonia decomposition, porous anodic alumina, microreactor, ruthenium, microreactor

Introduction

Recently, there has been considerable interest in building small hydrogen generators to power fuel cells for laptop computers and other portable electronic devices (Call, 2002; Neale, 2000; Srinivasan et al., 1997). So far, most designs have used conventional supported catalyst powders. However, catalyst pellets are not likely to withstand mechanical shaking in these applications. Powdered catalysts may clump in a way that leads to fluid bypassing, and poor heat transfer through powders can lead to unacceptably nonuniform temperature distributions. Bare metals and catalyst washcoats have been used to avoid one or more of these problems (McCreedy, 2000; Srinivasan et al., 1997), but surface areas per unit reactor volume have remained unacceptably low. In the case of washcoats, the low useful area persists despite high specific surface areas because washcoats can be made no more than a few microns thick (Watanabe et al., 2001; Wu et al., 2001).

In this article, we demonstrate the use of monolithic anodized aluminum posts as an alternative catalyst support. Posted reactors, such as that shown in Figure 1, can support acceptable surface to volume ratios while withstanding considerable shaking, avoiding bypassing, and promoting temperature uniformity attributed to structural continuity. The posts also enhance mass transfer to catalytic surfaces under high flow conditions by acting as static mixers (Ihm and Ruckenstein, 1978).

Anodized alumina has already been shown to be a useful catalyst support in other applications (Ihm and Ruckenstein, 1978; Jessensky et al., 1998; Patermarakis and Pavlidou, 1994; Shawaqfeh and Baltus, 1998; Shizaki et al., 2001). This material can be fabricated with straight pores having well-controlled pore sizes. Surface areas can reach roughly 50 m^2/g with layer thicknesses up to 100 μm. Pore sizes average 50–100 nm, which is large enough to avoid significant mass transfer resistances for most catalytic reactions (Ihm and Ruckenstein, 1978). Mardilovich et al. (2000) showed that structures with high aspect ratios can be synthesized using anodic alumina. Wiessmeier and Hönicke (1996) suggested that aluminum anodization can be used to produce catalytic components for microreactors. At present, though, the field is sufficiently new that we know of no published experimental data that demonstrate this concept.

Correspondence concerning this article should be addressed to R. Masel at r-masel@uiuc.edu.

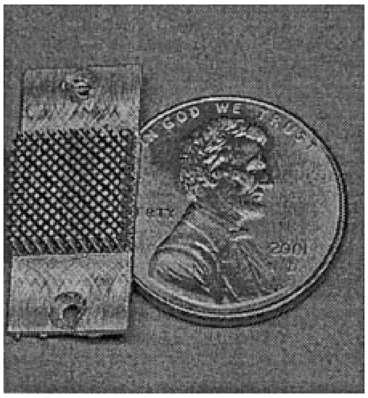

Figure 1. Posted catalyst structure sitting on a U.S. penny.

This device was used to make the measurements reported in Figures 5 and 6.

In the present study, we demonstrate the operation of a microreactor fabricated with anodized posts. We outline fabrication techniques and measure reactor conversion in the case of ammonia decomposition to hydrogen and nitrogen.

Materials and Methods

Catalyst structures were fabricated from rolled bar stock of 1100 aluminum (99+% Al) or 6061 aluminum (98+% Al, 0.5% Si, 0.4% Mg). Electrical discharge machining (EDM) was used to cut an array of approximately 250 square posts, each 300 μm wide and 3 mm high. The posts were arranged over a square area 9.5 mm wide. The resultant structures were degreased in acetone and anodized potentiostatically in 0.16 M oxalic acid solution for 24 h. The anodization voltage was varied in some cases to test the effects on the properties of the anodic alumina. The alumina was impregnated with a saturated solution of ruthenium (III) acetylacetonate in 2-pentanedione. The catalyst was then calcined for 6 h in air at 550°C, followed by reduction in hydrogen for 2 h at the same temperature.

After the catalyst was prepared, performance tests were done in a stainless steel tube heated by a temperature-controlled tube furnace. A few alumina pellets placed upstream of the reactor housing served as a reactant preheater. Effluent concentrations were monitored by leaking reactor effluent into an Extrel C-50 quadrupole mass spectrometer system to a pressure of 10^{-7} Torr from a base chamber pressure of 10^{-9} Torr. The mass spectrometer was calibrated by passing known mixtures of ammonia, hydrogen, and nitrogen through the reactor bypass. Control experiments throughout the temperature range of interest showed that the reactor housing induced no conversion in the absence of catalyst.

The flow of technical grade (99.99%) anhydrous ammonia was controlled using calibrated mass flow meters. All experiments were carried out with the reactor vented to the atmosphere.

Results

Effects of anodization conditions

Figure 2 shows optical microscope images of the reactor posts as a function of anodization conditions. Figure 2a shows the posts of an 1100 aluminum reactor before anodization. The posts are 300 μm wide, with 260 μm gaps among them. Figure 2b shows the posts of this kind of reactor after anodization at 30 V for 24 h at 30°C. The post size remains largely unchanged, but the posts become sheathed by a uniform, conformal layer of alumina about 60 μm thick. Figure 2c shows the effects of increasing the anodization voltage to 60 V. The alumina layer has cracked and fallen away at the corners of each post. The overall post width increases to 337 μm, with the interpost gaps decreasing to 223 μm. Figure 2d shows the effects of changing to 6061 aluminum under the anodization conditions of Figure 2b. The post size decreases to 254 μm, with the interpost gap increasing to 306 μm. There is no evidence of alumina within the resolution ($\sim$ 5 μm) of the measurement.

Figure 3 shows scanning electron microscope (SEM) images of cross sections of the anodized 1100 alumina posts in Figure 2. The posts were prepared for imaging simply by cutting with a razor blade. The posts anodized at 30 V cut smoothly with the alumina clearly adherent. By contrast, the posts anodized at 60 V snap off and show significant alumina cracking.

Figure 4 shows SEM micrographs of alumina microstructure. Figure 4a shows 1100-derived alumina anodized at 30 V. The pore diameters average approximately 50 nm. Figure 4b shows that increasing the voltage to 60 V increases the pore diameter to about 100 nm. Figure 4c shows the effect of changing to 6061-derived alumina at 30 V. The surface shows a thin porous oxide in some locations, but bare metal can also be seen where the anodic alumina coating has flaked away.

Surface area

BET measurements showed that 1100-derived alumina anodized at 30 V had a surface area of about 35 cm^2 per post. This figure corresponds to about 16 m^2/g in the anodized layer, and represents a factor of 900 increase from the bare metal surface area. Increasing the anodization voltage to 60 V decreases the area per post to about 26 cm^2, which is still a factor of 660 increase from the bare metal surface area.

Reactor conversion measurements

Figure 5 shows the fraction of ammonia converted to products using the 30-V anodized 1100 aluminum reactor at a constant ammonia flow rate of 15.0 sccm (standard cm^3/min). As expected, the conversion rises with increasing temperature, reaching 85% at 650°C. Figure 6 shows the fraction of ammonia converted as the flow rate is varied while holding the reactor at a constant temperature of 650°C. The conversion lies near 100% at low flow rates, dropping to about 40% at a high flow rate of 145 sccm.

We have also examined the posts at the end of the reaction for evidence of degradation from corrosion, temperature, or thermocycling. Generally, the posts anodized at 30 V are still intact after being heated to 650°C and cooled several times, although they do degrade if the reactor is heated above 650°C.

Discussion

The results show that anodization voltage needs to be chosen carefully to obtain adherent alumina layers. The adhesion behavior seems to be associated with the geometry of the struc-

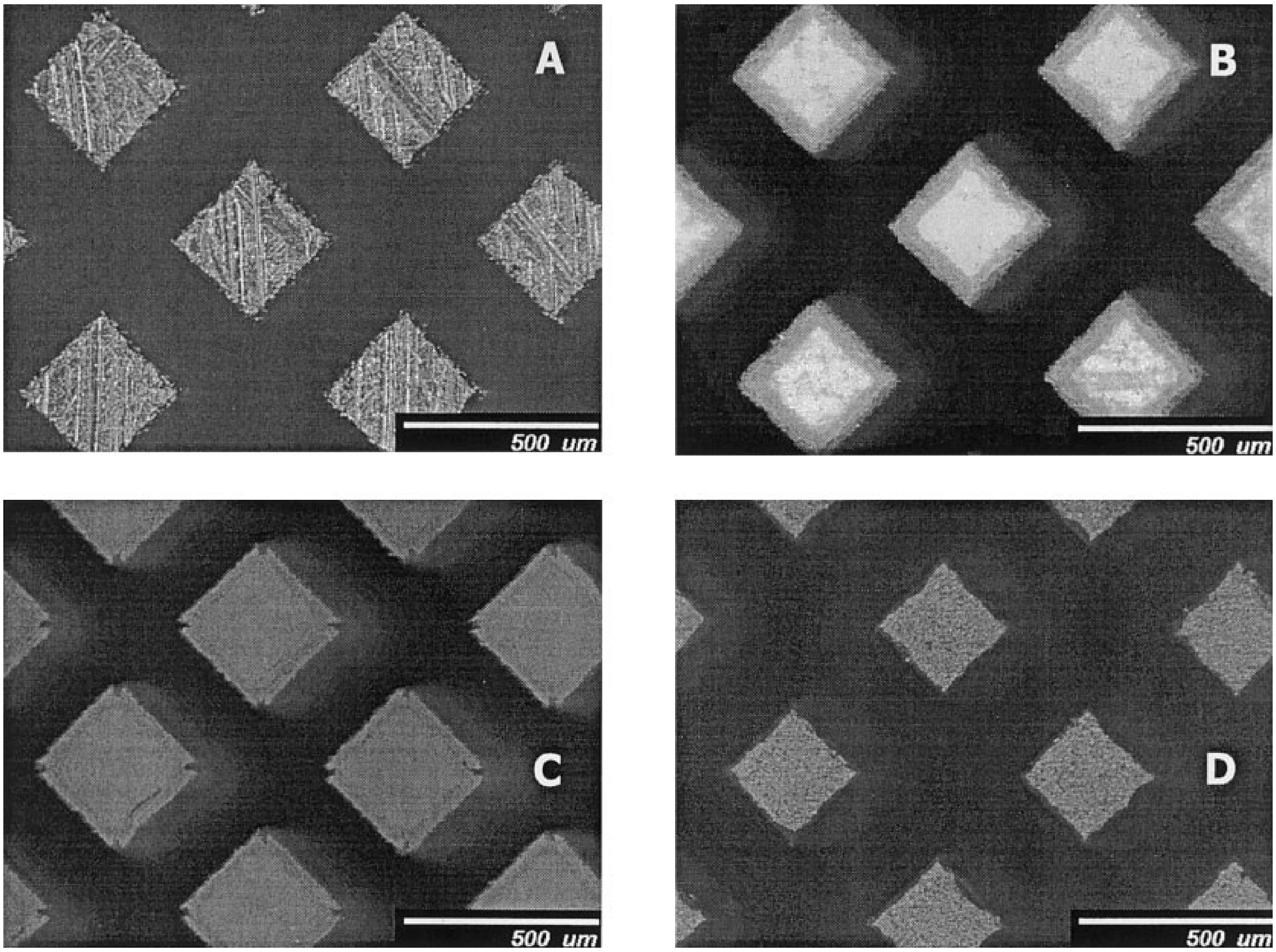

Figure 2. Optical microscope images of microreactor posts made from 1100 Al alloy (A) before anodization; after anodization for 24 h at 30°C and (B) 30 V and (C) 60 V: conditions in (D) were the same as in (B) except that 6061 Al alloy was used.

ture. For example, Patermarakis and Pavlidou (1994) anodized flat foils under the same conditions used make the posts in Figure 4b, yet obtained adherent films. We have reproduced this result for both Al foils and flat 1100 Al bars.

The following scenario may explain the difference. Anodization involves both expansion of the alumina attributed to oxidation and shrinkage of the substrate attributed to metal dissolution. Stresses will build up at the post corners unless the layers growing in perpendicular directions grow at the same rate. These stresses can induce delamination. In the present work, structures stable to heating formed only when the post dimension remained constant during the anodization, meaning that dissolution and expansion balanced exactly. Unfortunately, the conditions where such a balance holds do not necessarily correspond to the conditions that optimize the surface area of the structures.

Although the surface areas reported here are substantial, they are not as high as those reported previously reported for anodized foils. Our anodization of 1100 aluminum at 30 V produced only 60 μm of alumina with a specific area of 16 m^2/g, between half and a third of the specific surface areas found elsewhere (Ihm and Ruckenstein, 1978; Jessensky et al., 1998; Patermarakis and Pavlidou, 1994; Shawaqfeh and Baltus, 1998; Shizaki et al., 2001; Wu et al., 2001). Alumina thicknesses up to a factor of 2 more than ours have also been reported for Al foils (Patermarakis and Pavlidou, 1994). The net reduction is a factor of 4 to 6 in available surface area per unit of exposed post area.

Still, the support surface areas obtained with respect to substrate surface area are larger than those reported previously for nonporous substrates washcoated with alumina or silica (McCreedy, 2000; Watanabe et al., 2001). They also are much larger than those seen with metal coatings. Thus, although the surface areas are still modest compared to typical commercial supported catalysts (150 m^2/g), the surface areas are quite substantial compared to the catalytic structures used previously in microreactors.

We also observe considerable catalytic activity. Figures 5 and 6 show that ammonia is converted at substantial rates. At a feed rate of 50 sccm, roughly 46 sccm of hydrogen was produced, corresponding to an available power of about 13 W for a fuel cell. This power is almost sufficient for a laptop

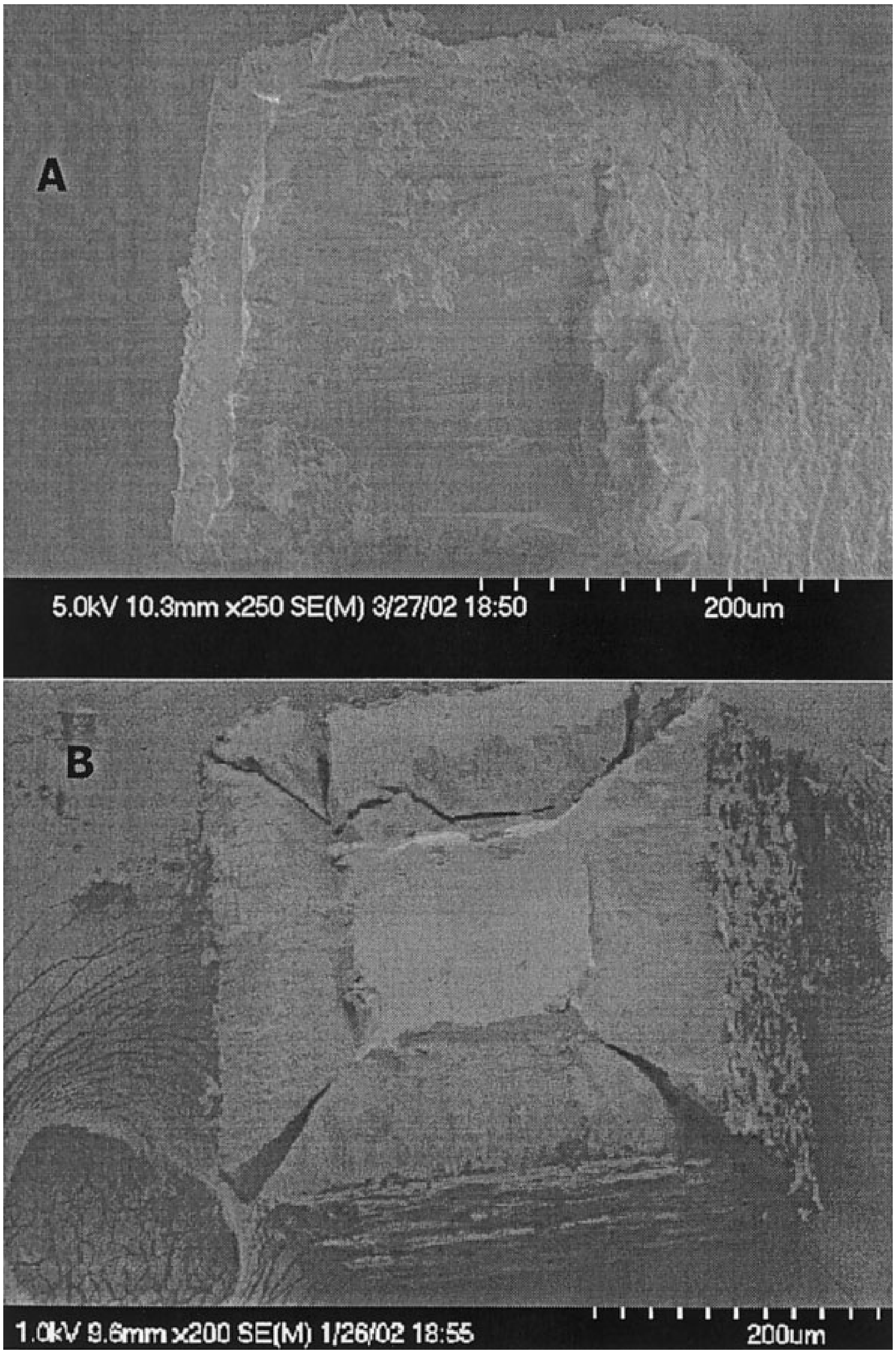

Figure 3. SEM micrographs of cutaway view of 1100 alloy post anodized for 24 h at (A) 30 V and (B) 60 V.

computer, yet the catalyst bed is a third the area of a penny and only about three times thicker.

Conclusions

We have demonstrated, for the first time, that arrays of monolithic anodized aluminum posts are useful catalyst supports for microreactors. The posted structures stay in place in the microreactor, and they do not suffer from the fluid bypassing that plagues other previous microreactor designs. The surface areas are modest compared to supported catalysts, but large compared to the bare metal and washcoated monolithic microreactor designs. The structures have shown the ability to withstand significant thermocycling, and show substantial catalytic activity when impregnated with metal. In particular, we have demonstrated the production of 13 W of hydrogen by decomposition of ammonia. Clearly, there is more work to be

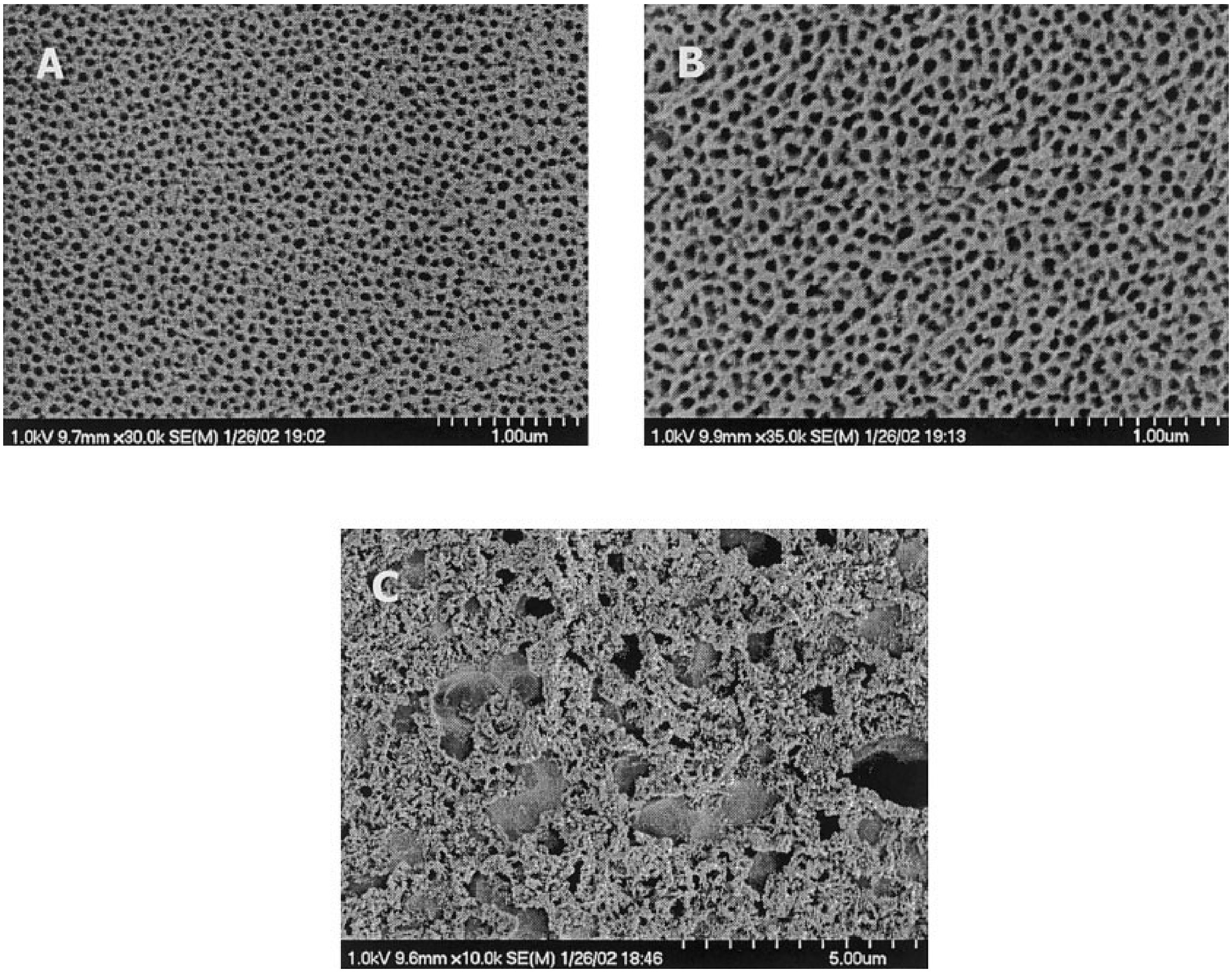

Figure 4. SEM micrographs of anodized posts: pores in alumina layer on 1100 Al after anodization for 24 h at (A) 30 V and (B) 60 V: conditions in (C) are equivalent to (A) except that 6061 Al was used.

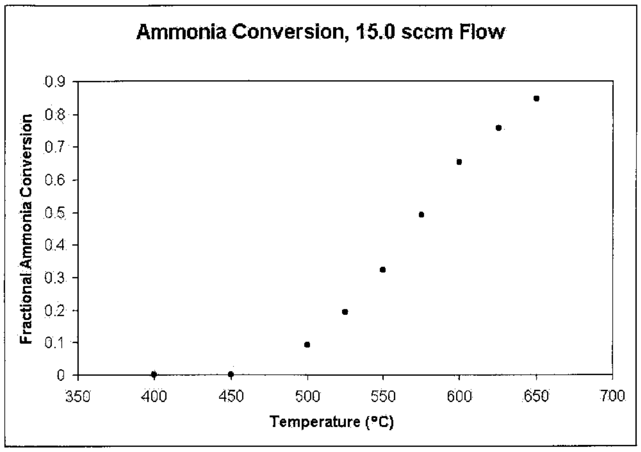

Figure 5. Fractional ammonia conversion (30 V anodization, 1100 alloy) vs. reactor temperature.

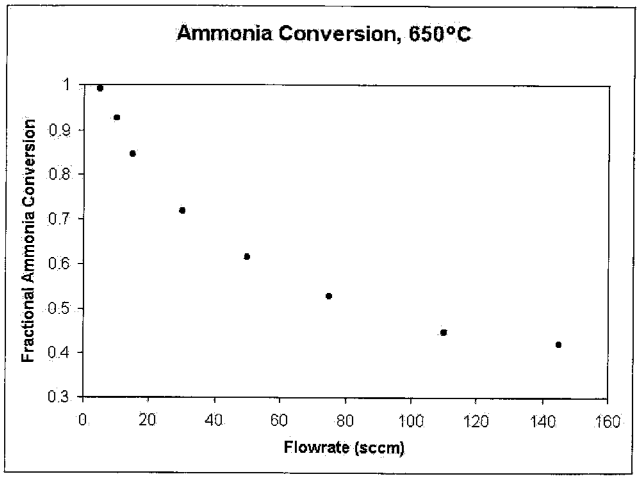

Figure 6. Fractional ammonia conversion (30 V anodization, 1100 alloy) vs. ammonia feed flow rate.

done in terms of increasing support surface area with improved anodization techniques and reactor geometry, but these results show promise.

Acknowledgments

This work was supported by the Department of Defense Multidisciplinary University Research Initiative (MURI) program administered by the Army Research Office under Contract DAAD19-01-1-0582. The authors also thank Dr. Kenneth Suslick for assistance in the BET surface area measurement of reactor samples, and Dr. Vania Petrova of the DOE Center for Microanalysis of Materials at UIUC for assistance in SEM imaging of the reactor posts.

Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the Department of Defense or the Army Research Office.

Literature Cited

Call, C., *Proc. Palm Power Workshop*, Panama City, FL, Mar. 2002.

Ihm, S., and E. Ruckenstein, "Porous Catalysts with No Diffusional Limitation-Reaction Rates," *Ind. Eng. Chem. Prod. Res. Dev*., **17**(2), 110 (1978).

Jessensky, O., M. F. Müller, and U. Gösele, "Self-organized Formation of Hexagonal Pore Arrays in Anodic Alumina," *Appl. Phys. Lett.*, **72**(10), 1173 (1998).

Mardilovich, P., D. Routkevitch, and A. Govyadinov, "New Approach for Surface Microstructuring," *MEMS*, **2**, 45 (2000).

McCreedy, T., "Fabrication Techniques and Materials Commonly Used for the Production of Microreactors and Micro Total Analytical Systems," *Trends Anal. Chem.*, **19**, 396 (2000).

Neale, R., "Motorola Move Communications Towards the Miniature Fuel Cell," *Electronic Eng.*, **72**, 9 (2000).

Patermarakis, G., and C. Pavlidou, "Catalysis over Porous Anodic Alumina Catalysts," *J. Catal.*, **147**, 140 (1994).

Shawaqfeh, A., and R. Baltus, "Growth Kinetics and Morphology of Porous Anodic Alumina Films Formed Using Phosphoric Acid," *J. Electrochem. Soc.*, **145**(8), 2699 (1998).

Shizaki, S., T. Hosoda, M. Sakurai, H. Kameyama, and I. Nagashima, "Evaluation of the Selectivity for Methanol Decomposition over Anodized Aluminum Plate Catalyst Coated with Silica," *J. Chem. Eng. Japan*, **34**(10), 1229 (2001).

Srinivasan, R., I. M. Hsing, P. E. Berger, K. F. Jensen, S. L. Firebaugh, M. A. Schmidt, M. P. Harrold, J. J. Lerou, and J. F. Ryley, "Micromachined Reactors for Catalytic Partial Oxidation Reactions," *AIChE J.*, **43**, 3059 (1997).

Watanabe, K., M. Sakairi, H. Takahashi, K. Takahiro, S. Nagata, and S. Hirai, "Anodizing of Aluminum Coated with Silicon Oxide by a Sol-Gel Method," *J. Electrochem. Soc.*, **148**, B473 (2001).

Wiessmeier, G., and D. Hönicke, "Microfabricated Components for Heterogeneously Catalysed Reactions," *J. Micromech. Microeng.*, **6**, 285 (1996).

Wu, X., D. Weng, L. Xu, and H. Li, "Structure and Performance of Gamma-Alumina Washcoat Deposited by Plasma Spraying," *Surf. Coat. Technol.*, **145**, 226 (2001).

Manuscript received Apr. 26, 2002, and revision received July 25, 2003.