

# Hydrophilic and Antimicrobial Zeolite Coatings for Gravity-Independent Water Separation\*\*

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Condensing heat exchangers onboard manned spacecraft require hydrophilic fin surfaces to facilitate wetting and wicking of condensate to achieve gravity-independent water separation in the zero- or micro-gravity environment of space. In order to prevent the proliferation of microbes, the coating must also be biocidal. Here we show for the first time that zeolite A and ZSM-5 coatings deposited via in-situ crystallization on stainless steel and aluminum alloys have excellent hydrophilicity, biocidal properties, and adhesion. Water contact angles below 5° were obtained on most substrates tested. When silver-ion exchange is carried out on the zeolite A coating, it becomes highly antibacterial. This biocidal capability of zeolite A is regenerative by repeated ion exchange. All coatings exhibit the highest rating of 5B as determined by adhesion test ASTM D-3359-02 (American Society for Testing and Materials). These properties, in addition to zeolite coating's low-temperature crystallization process and demonstrated corrosion resistance, make zeolite coatings advantageous over the current sol-gel coatings and well suited for use in condensing heat exchangers onboard manned spacecraft.

## 1. Introduction

Condensing heat exchangers (condensers) are a key component in the environmental control systems (ECS) onboard manned spacecraft, and, similar to their ubiquitous ground-based counterparts for vehicles and buildings, their function is to regulate temperature and humidity.<sup>[1-4]</sup> To realize effective water separation in the zero- or micro-gravity environment, however, these space-based condensers are required to have a hydrophilic coating on their air-side fin surfaces. The function of this coating is to attract the water condensate into a film on the fin surfaces so that vacuum can be used to sip the water away through the so-called "slurper" holes.<sup>[1]</sup> If the fin surface is hydrophobic, the water condensate tends to stay in droplet form, and if these droplets are not strongly attached to the fin surfaces they can become entrained in the air stream and blown back to the crew cabin, causing fog or rain. If these droplets are strongly attached to the fin surfaces, they can cause "bridging" of the air pathways, leading to a significant increase in pressure drop and fan power consumption.

At present, the most commonly used and studied hydrophilic and antimicrobial coatings are sol-gel-based inorganic oxide coatings such as silica and alumina.<sup>[3,4]</sup> This type of coating is usually applied by wash-coating or dip-coating, a method

widely used for preparing heterogeneous catalysts on monolithic supports (e.g., automotive three-way exhaust catalysts). A typical wash-coating process consists of slurry preparation, slurry application by washing or dipping, air knifing, drying, and sintering. To make the slurry, multiple components (i.e., hydrophilic agent, binder, antimicrobial agent, and dispersant) are required and yet they interact with little synergetic effect. For example, very often the binder and the antimicrobial agent are hydrophobic in nature, and thus the composition of the slurry is a delicate balance between hydrophilicity, good adhesion, and long-lasting antimicrobial function, leading to non-optimal performance with respect to hydrophilicity, adhesion, and service life.

The wash-coating method also has several other significant limitations. For example, for very small wavy fins (e.g., 28 fins/inch (one inch = 2.54 cm)), excessively strong air knifing tends to leave some fin surfaces uncoated while weak air knifing leads to clogged fins. Once the wet coating is formed, it has to be dried and sintered at high temperatures (e.g., 300–600 °C) to establish binding among the coating components and adhesion between the coating and the fin surface. However, this high-temperature treatment is highly undesirable because it often adversely affects the mechanical properties of the condenser alloys.

Because of the constant presence of water on the surface of the condensers, microbial growth is likely.<sup>[3,4]</sup> Thus, an antimicrobial function is needed. The antimicrobial agent in the sol-gel coating is included (usually an oxide, e.g., silver oxide) in the slurry and released by their natural dissolution into water. Once the antimicrobial agent is depleted, the coating must be stripped and the condenser re-coated. This means that the antimicrobial function is not regenerative.

Furthermore, the sol-gel coatings are highly porous and the pores are typically large (e.g., micrometer or sub-micrometer-sized). Although this porosity helps to adsorb and wick water, it does not provide corrosion resistance to the metal substrate.

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Corrosion concerns have been the primary reason that current condensers used in space applications are made of steels. A corrosion-resistant coating would allow use of aluminum alloys in place of stainless steels in the condensers. Since aluminum is lighter and has higher heat conductivity than steels, this switch would lead to significant weight and volume reduction.

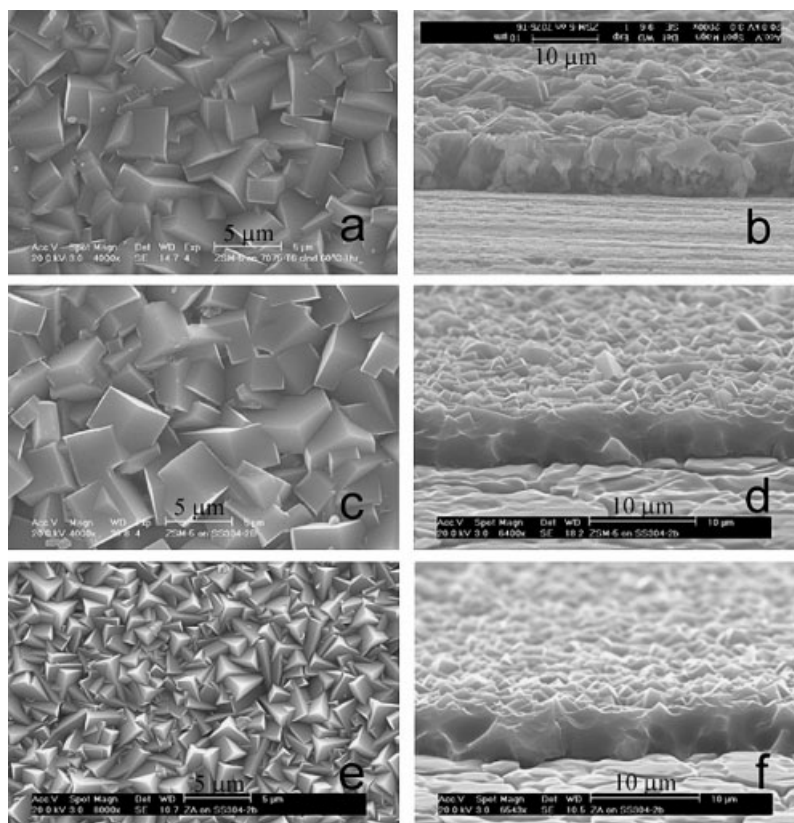
We have been interested in developing hydrophilic and antimicrobial zeolite coatings for use in manned spacecraft. Zeolites are crystalline aluminosilicates with uniform molecular sized pores. At present, major commercial uses of zeolites include catalysts, separation media, and ion exchangers. For these applications they are used in powder composite form such as pellets and granules. We have previously demonstrated that ZSM-5 coatings in their as-synthesized state are extremely corrosion-resistant in strong acid, base, and pitting-aggressive solutions, and the in-situ crystallization process is a simple low-temperature (e.g., 165 °C) one-step process that can coat surfaces of complex geometry and in confined space.<sup>[5]</sup> In this study, we show for the first time that zeolite coatings (ZSM-5 and zeolite A) can be highly hydrophilic and antimicrobial and are promising for use in space applications. We also show that these coating have excellent adhesion to all substrates tested. In addition, the coatings tested had a thickness of only 4–6 μm, nearly one hundred times thinner than the current technology, thus allowing for a significant reduction in pressure drop across the condenser.

## 2. Results and Discussion

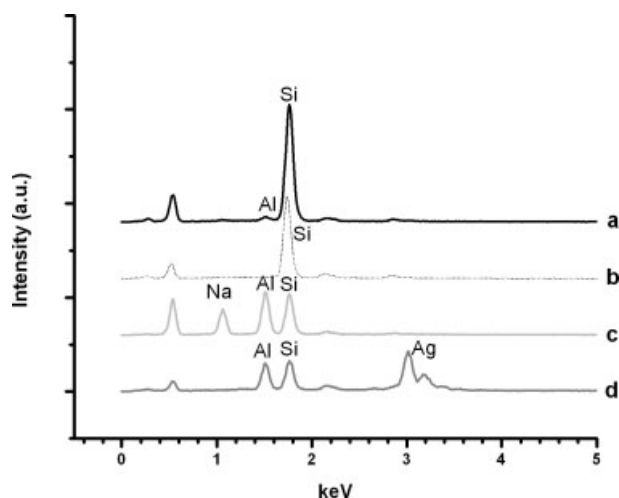
ZSM-5 and zeolite A coatings on aluminum alloys (AA-2024-T3, AA-5052-H32, AA-6061-T4, and AA-7075-T6) and stainless steel (SS-304-2B) exhibited complete and even coverage over the entire substrate surface. Scanning electron microscopy (SEM) images for ZSM-5 on AA-7075-T6, a likely choice of aluminum alloy for condensers, and SS-304-2B, and zeolite A on SS-304-2B are shown in Figure 1. Clearly, polycrystalline coatings have been formed and they are fully inter-grown and approximately 4–6 μm thick.

Semiquantitative elemental analysis presented in Figure 2 shows that ZSM-5 (Figs. 2a,b) has much higher silicon-to-aluminum ratios than zeolite A (Figs. 2c,d). After submersion in 0.01 M silver nitrate, the sodium ions in the pores of the zeolite A coating are replaced by silver ions (Figs. 2c,d). It is the silver ions in the pores of the zeolite A that give this coating the antibacterial properties described below.

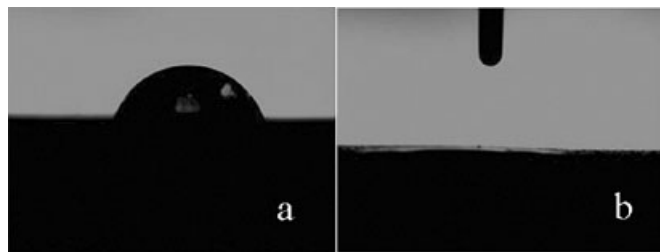
The hydrophilicity of the coatings was evaluated using contact-angle measurements. For many of the ZSM-5 and zeolite A-coated coupons, the drop was wicked away by the hydrophilic surface so quickly that it was impossible to obtain a measurement from these images. To facilitate the measurement of contact angles on these very hydrophilic surfaces, images were taken within the first few seconds after the dispensed drop contacted the substrate (Fig. 3). (Figure 4 shows the typical decrease in contact angle after coating stainless steel with a



**Figure 1.** SEM images of a,b) ZSM-5 on AA-7075-T6; c,d) ZSM-5 on SS-304-2B; and e,f) zeolite A on SS-304-2B. (a,c,e) are top views and (b,d,f) are cross-sectional views.



**Figure 2.** Semiquantitative elemental analysis by EDAX of a) ZSM-5 on AA-7075-T6; b) ZSM-5 on SS-304-2B; c) zeolite A on SS-304-2B and d) zeolite A on SS-304-2B after silver-ion exchange.

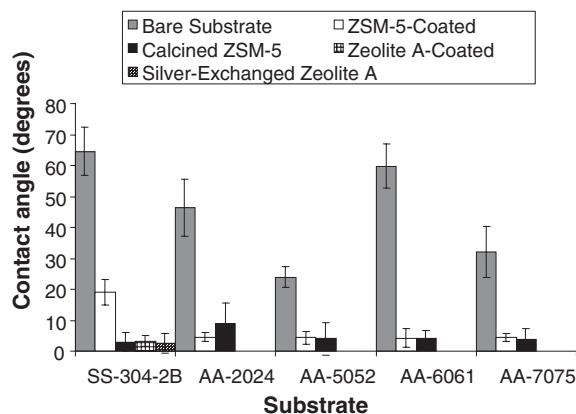


**Figure 3.** Water contact angle comparison between a) bare SS-304-2B and b) the same substrate coated with zeolite A.

zeolite A thin film. The ability of the zeolite A coating to wick water on the surface into a film is clearly demonstrated.

Quantitatively, coating substrates with ZSM-5 resulted in 71–93 % reductions in contact angles from the bare substrate for all aluminum alloy and stainless-steel substrates tested (Fig. 4). Calcination either slightly improved the hydrophilicity of ZSM-5-coated coupons or had no significant effect. Average contact angles for ZSM-5 before and after calcinations were all below 10° except for the uncalcined ZSM-5 coating on SS-304-2B, which was measured at  $19 \pm 4^\circ$ . Average contact angles were below 5° on zeolite A-coated stainless steel both before and after silver-ion exchange. As expected, zeolite A is more hydrophilic than ZSM-5 because of the lower silicon-to-aluminum ratio. With contact angles below 30°,<sup>[3]</sup> these surfaces are all classified as hydrophilic and would be highly effective at performing the wetting and wicking function required in condensing heat exchangers onboard manned spacecraft.

The American Society for Testing and Materials (ASTM) cross-cut tape test for adhesion<sup>[6]</sup> demonstrates the strong adhesion of ZSM-5 and zeolite A to all the types of substrates tested. Presented in Table 1 are the results of the adhesion testing. All ZSM-5 coatings, as-synthesized or calcined, exhibited the highest adhesion rating of 5B on all substrates tested. Zeolite A on stainless steel flaked slightly along the cuts made in the coating and yielded a rating of 4B. Although not required



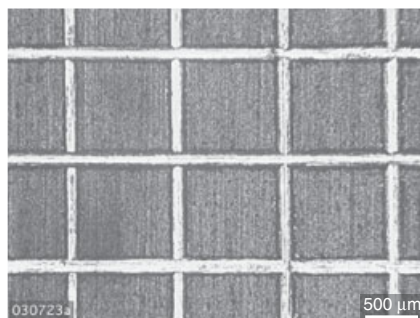
**Figure 4.** Contact-angle comparison between bare substrates and those coated with a zeolite thin film.

**Table 1.** Adhesion performance of coatings as determined by ASTM D 3359B-02.

Substrate	Coating	Adhesion rating
AA-2024-T3	ZSM-5	5B
AA-2024-T3	Calcined ZSM-5	5B
AA-5052-H32	ZSM-5	5B
AA-5052-H32	Calcined ZSM-5	5B
AA-6061-T4	ZSM-5	5B
AA-6061-T4	Calcined ZSM-5	5B
AA-7076-T6	ZSM-5	5B
AA-7076-T6	Calcined ZSM-5	5B
SS-304-2B	ZSM-5	5B
SS-304-2B	Calcined ZSM-5	5B
SS-304-2B	Zeolite A	4B

by the ASTM test protocol, the tested samples were also analyzed under a high-resolution polarized-light microscope to provide a more critical look at the adhesion of each coating and the typical result for as-synthesized ZSM-5 on AA-7075-T6 is shown in Figure 5. These pictures (other not shown) reveal no removal of ZSM-5 from AA-5052-H32, AA-6061-T4, AA-7075-T6, and SS-304-2B along sides of the cross-cuts. Calcined ZSM-5 on all types of substrates had excellent adhesion with no visible flaking of the coating under the polarized-light microscope. It is believed that the strong adhesion between ZSM-5 and aluminum alloy is due to the incorporation of aluminum from the substrate into the ZSM-5 framework. Similar incorporation of iron from stainless steel to zeolite framework is also possible, although the extent of incorporation is expected to be less than for aluminum.

Figure 6 contains the results of the test for antibacterial efficacy of silver-exchanged zeolite A coatings. Samples were initially inoculated with 500  $\mu\text{L}$  of a bacterial suspension containing more than  $1 \times 10^6$  cfu (cfu: colony-forming units). Three samples of each substrate type were enumerated immediately after inoculation. These immediate enumerations yielded cell counts of greater than  $1 \times 10^6$  cfu on the bare stainless steel and zeolite A-coated stainless steel, and an average of 13 cfu for silver-exchanged zeolite A-coated stainless steel. It is thought that the silver-exchanged zeolite A coating was able to kill bac-



**Figure 5.** Polarized-light microscope image of ZSM-5 coating AA-7075-T6 after a cross-cut adhesion test by the ASTM standard D 3359-02, Method B.



**Figure 6.** Surviving colony-forming units on bare stainless steel, zeolite A-coated stainless steel, and silver-ion-exchanged zeolite A over a 24 h incubation period.

teria on contact.

Subsequent cell counts after incubation show a further decline in the number of viable cells on the silver-exchanged coating after 4 h. After 24 h of incubation on top of the silver-exchanged zeolite A there were no surviving cfu. A parallel incubation of *E. coli* on bare stainless-steel coupons yielded a greater than ten-fold increase in the number of cfu after 24 h, while zeolite A-coated coupons had an approximately ten-fold decrease in cfu after the same amount of time. These results demonstrate that the silver-exchanged zeolite A is extremely effective at killing a large number of cells over a short amount of time. Although the zeolite A coating without silver does not have any biocidal capabilities, its hydrophilicity may have allowed some cells to adhere to the coating instead of being transferred to the buffer solution for enumeration, explaining the slight decline in the number of counted cfu.<sup>[7]</sup>

### 3. Conclusions

This study demonstrates that zeolite thin films grown via an in-situ crystallization process possess the characteristics necessary for use in condensers on board manned spacecraft. The coatings produced are highly hydrophilic, allowing them to

wick water away from the metal surfaces. The coatings created have excellent adhesion to the stainless-steel and aluminum-alloy substrates. After silver-ion exchange, zeolite A has high antimicrobial efficacy. Silver is not considered toxic to humans, and the antimicrobial capability is obviously regenerative. These characteristics plus the fact that as-synthesized high-silica-content ZSM-5 is highly corrosion resistant make zeolite an excellent alternative to technology currently being used in condensers onboard manned spacecraft.

### 4. Experimental

**Preparation of Coated Coupons:** Stainless steel (SS) and aluminum alloy (AA) coupons with the dimensions 2 cm × 3.5 cm were submerged in a 1.3 wt.-% solution of Alconox detergent (Alconox, Inc.) for 1 h for cleaning. AA-2024-T3 and AA-7075-T6 substrates were cleaned at 60 °C while AA-5052-H32, AA-6061-T4 [9], and SS-304-2B were cleaned at 80 °C. The coupons were then rinsed and wiped clean under running de-ionized (DI) water with gloved hands. After drying with compressed air, the coupons were stored in sterile 50 mL centrifuge tubes until zeolite coating deposition or direct use in subsequent tests.

A ZSM-5 synthesis solution was prepared with a molar composition of 16 TPAOH:0.64 NaOH:1 TEOS:92 H<sub>2</sub>O:0.0018 Al, where TPAOH and TEOS stand for tetrapropylammonium hydroxide and tetraethyl-orthosilicate, respectively. Aluminum powder was mixed in water and then sodium hydroxide added. This solution was stirred for 30 min at room temperature. TPAOH and the remaining water were added and the solution stirred for an additional 15 min. TEOS was then added drop-wise to the solution and allowed to stir for at least 4 h. The desired substrates were then submerged vertically in the synthesis solution inside sealed Teflon-lined autoclaves (Parr Instrument Co., Moline, IL) and heated in a convection oven at 175 °C for 15 h. The coated substrates were washed under DI water and dried with compressed air. Some coated samples were calcined at 350 °C for 8 h to remove the structure-directing agent (SDA), TPAOH, from the pores of the zeolite coating.

The zeolite A synthesis solution with the molar composition of 10 Na<sub>2</sub>O:0.2 Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub>:200 H<sub>2</sub>O was prepared by first combining aluminum powder (200 mesh, 99.95+ %, Aldrich) and DI water in a 500 mL polypropylene bottle and stirring for about 10 min. Next, the full amount of sodium hydroxide was added and the bottle quickly capped. After stirring for an additional 30 min, Ludox LS30 colloidal silica (30 wt.-%, silica, Aldrich) was added drop-wise to the stirring solution. The synthesis solution was stirred for approximately 4 h until it became clear. Polypropylene balls (2 cm diameter) were slit with a razor blade and individual stainless-steel coupons inserted into these slits. The coupons with the balls attached were then floated in 250 mL wide-mouth polypropylene bottles containing 100 mL of the zeolite-A solution. After thermal treatment at 65 °C for 15 h, the coupons were removed and washed thoroughly under DI water. Compressed air was blown over the coupons to facilitate drying.

Zeolite A-coated samples were given their antibacterial property by an ion exchange with silver salt. This was carried out by submerging the zeolite A-coated coupons in a gently stirred 0.01 M solution of AgNO<sub>3</sub> in an amber colored or covered bottle at room temperature for 6–8 h. After this time, coupons were thoroughly washed with DI water and allowed to soak in DI water for 1 h. The coupons were dried with compressed air, making them ready for testing.

**X-Ray Diffraction, Scanning Electron Microscopy, and Contact-Angle Measurements:** Samples of the coated coupons were analyzed using X-ray diffraction (XRD, Siemens D-500 diffractometer using Cu K $\alpha$  radiation) to verify the formation of the expected zeolite. Scanning electron microscopy (SEM, Philips XL30-FEG operating at 20 kV) images and elemental analysis of the coating using energy-dispersive analysis of X-ray (EDAX) were also obtained for each type of zeolite.

The contact angles of all the different substrates and coatings were measured using the VCA-Optima (AST Products, Inc.). The coupon was loaded onto the sample stage and the motorized syringe dispensed a 0.2  $\mu\text{L}$  drop of DI water. The sample stage was then raised until the coupon came into contact with the water drop suspended from the syringe tip. After contact was made, the sample stage was lowered and the contact angle measured with the VCA image analysis software. Twelve measurements were made on each sample and three samples of each type were analyzed. Data is reported as averages with an error corresponding to the standard deviation between measurements.

**Adhesion:** Adhesion of the zeolite films to the various substrates was measured according to American Society for Testing and Materials (ASTM) ASTM D 3359B-02.<sup>[6]</sup> The adhesion test kit was purchased from the Paul N. Gardner Company, Inc., Pompano Beach, FL. The cutting tool was fitted with a blade containing eleven teeth spaced 1.0 mm apart. Coated coupons were secured to the lab bench by a c-clamp and the cutting tool was used to make the cross-cut pattern at 90° angles through the coating. The coating was brushed lightly with a soft brush after each cut to remove excess debris from the surface. Permacel 99 tape was applied to the cut surface and rubbed with the eraser on the end of a pencil to ensure good contact with the coating and then removed after 90 se. Samples were evaluated under a lighted magnifying glass (7 $\times$ ) and rated according to the ASTM rating scheme. The cut samples were also examined with a high-magnification microscope (Nikon Microphot-FXA).

**Antimicrobial-Function Measurements:** The biocidal function was tested following published protocols [8]. *E. coli* (JM 109) was taken from frozen stock at -80 °C and cultured overnight in Luria-Bertani (LB) medium at 37 °C. After overnight incubation, the culture was centrifuged and the LB broth was removed. The cells were washed and re-suspended in Butterfield's Buffer (BFB) (Intl. Bioproducts) to an optical density (OD) at 540 nm between 0.1 and 1.0. Further dilutions were made to obtain the desired cell concentration for inoculation onto the coupons.

Aliquots (6.5 mL) of BFB were pipetted into sterile Petri dishes. In these Petri dishes, single SS-304-2B coupons (bare, zeolite A-coated, and silver-exchanged zeolite A-coated) were placed upon sterile Teflon stands so that the coupons were supported above the BFB. Individual coupons were inoculated with 500  $\mu\text{L}$  of BFB containing greater than  $1 \times 10^6$  colony-forming units (cfu) of *E. coli*. The bacteria were allowed to incubate on the coupons for 4 and 24 h at 37 °C at a constant relative humidity of 60 %. After this time, the Teflon supports were removed

and the incubated coupons were transferred into the BFB at the bottom of the Petri dishes and swirled gently. To insure adequate transfer of the cells into the BFB, the surface of each coupon was scraped with a sterile cell spreader (Fisher Scientific) three times along the major axis of the coupon and then three more times along the minor axis. An additional 3 mL of BFB was used to rinse the coupon and the cell spreader, bringing the total volume in the Petri dish to 10 mL. The rinsed coupons were then removed and the buffer solution diluted for enumeration. In order to determine how many cfu were initially inoculated onto the coupons, three samples of each type of coupon were processed immediately after inoculation using the same methods just described.

The bacterial suspension containing the cells incubated on the coupons was serially diluted to the appropriate concentration for plating. 100  $\mu\text{L}$  aliquots of this diluted suspension were then dispensed onto an LB agar medium, spread, and incubated for 24 h at 37 °C. Colony-forming units were counted visually and used to back-calculate the total number of cfu surviving on the coupons after the respective incubation times.

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- [1] J. C. Fletcher, R. B. Trusch, E. W. O'Connor, *US Patent 3 868 830*, **1975**.
- [2] F. Petter, C. Planert, SAE Technical Paper Series, 901284, presented at 20th Int. Conf. on Environ. Syst., Williamsburg, VA, July 1990.
- [3] J. W. Steele, P. J. Birbara, T. D. Scull, *US Patent 5 305 827*, **1994**.
- [4] S. J. Zhou, M. R. Keyvan, G. Seminara, H. Pickup, *US Patent 6 102 994*, **2000**.
- [5] X. L. Cheng, Z. B. Wang, Y. S. Yan, *Electrochem. Solid-State Lett.* **2001**, *4*, B23.
- [6] American Society for Testing and Materials, ASTM, West Conshohocken, PA, D-3359-02 cross-cut tape test for adhesion.
- [7] H. Ai, Y. M. Lvov, D. K. Mills, M. Jennings, J. S. Alexander, S. A. Jones, *Cell Biochem. Biophys.* **2003**, *38*, 103.
- [8] M. M. Cowan, K. Z. Abshire, S. L. Houk, S. M. Evans, *J. Ind. Microbiol. Biotech.* **2003**, *30*, 102.
- [9] F. King, *Aluminum and Its Alloys*, John Wiley and Sons, New York **1987**.