Corrosion Protection

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Corrosion Resistance of Superhydrophobic Layered Double Hydroxide Films on Aluminum**

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The costs of metal corrosion amount to several percent of the GDP of an industrialized country.[1] In the case of aluminum, chromate-based coatings[2] provide highly effective corrosion protection, but environmental regulations are increasingly restricting their use. Anodization[3] increases the thickness of the oxide layer, but it retains its porous nature.[4] Layered materials such as anionic clays (e.g., layered double hydroxides)[5,6] and cationic clays (e.g., montmorillonite)[7] have been widely investigated as additives in organic anticorrosion coatings or as polymer–clay nanocomposite corrosion-resistant coatings. Zeolites[8,9] have also been explored as corrosion-resistant coating materials. Hydrophobic self-assembled monolayers (SAMs)[10] of surfactant molecules on the surface have recently been proposed as corrosion inhibitors but suffer from the drawbacks that the layers have limited stability and molecule-sized defects which allow water to reach the underlying surface. These problems should be mitigated if the surfactant could be incorporated in an inorganic host matrix, a thin film of which has been previously strongly bonded to the aluminum surface.

Layered double hydroxides (LDHs) are one such potential inorganic host. They can be expressed by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]\,A^{n-}_{x/n}\cdot m\,H_2O$, where the cations M^{2+} and M^{3+} occupy the octahedral holes in a brucite-like layer and the anion A^{n-} is located in the hydrated interlayer galleries.[11] The ability to vary the composition over a wide range allows materials with a wide variety of properties to be prepared. We recently showed[12] that an NiAl-LDH–CO_3^{2-} film can be formed directly on porous anodic alumina/aluminum (PAO/Al) substrates; since PAO/Al is the only source of Al^{3+}, the thin film grows directly on the substrate and thus exhibits good adhesion and mechanical stability.[13] Treatment with sodium laurate (*n*-dodecanoate) results in surface-bonded laurate films showing superhydrophobicity with water contact angles (CA) greater than 160°. Here we show that intercalation of laurate anions by ion exchange with ZnAl-LDH–NO_3^- film precursors on a PAO/Al substrate leads to a hierarchical micro/nanostructured superhydrophobic film which provides a very effective corrosion-resistant coating for the underlying aluminum.

The aluminum substrate was first coated with a layer of porous anodic alumina by conventional anodization and subsequently treated with an alkaline solution of zinc nitrate in the presence of an excess of nitrate anions. In addition to the peaks of the PAO/Al substrate, the XRD pattern of the film shows two low-angle reflections at 8.874 and 4.462 Å (Figure 1 a), which can be assigned to the [003] and [006] reflections of an LDH phase with a basal spacing of 0.887 nm, consistent with the literature for ZnAl-LDH–NO_3^-.[14] The presence of NO_3^- in the interlayer galleries of the LDH film was confirmed by the characteristic peak at 1384 cm^{-1} in the FTIR spectrum. It is well known that LDHs in their usual powder form readily exchange NO_3^- ions for other anions,[11] so the ZnAl-LDH–NO_3^- film should be a suitable precursor for organic-intercalated LDH films.

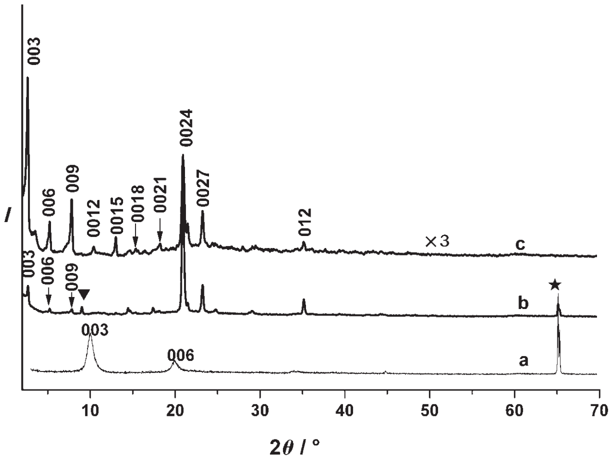

Figure 1. XRD patterns of a) ZnAl-LDH–NO_3^- precursor film, b) ZnAl-LDH–laurate hybrid film and c) ZnAl-LDH–laurate powder scraped from the hybrid film sample. ★ and ▼ indicate the reflection peaks from the PAO/Al substrate and sodium laurate, respectively.

Figure 1 b shows the XRD pattern of the ZnAl-LDH–NO_3^- film after reaction with a solution of sodium laurate, and that of the corresponding powder sample scraped from the substrate is shown in Figure 1 c. The series of low-angle peaks can be assigned to a basal reflection and higher order harmonics of a material with a basal spacing of 3.42 nm. This is consistent with the value expected for a bilayer of laurate anions arranged in a tilted orientation within the interlayer

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galleries.[15,16] (The XRD peak positions and relative intensities of the hybrid film are listed in the Supporting Information.) Incorporation of laurate anions was confirmed by the FTIR spectrum of the ZnAl-LDH–laurate powder scraped from the hybrid film, which showed two strong absorption bands at about 1410 and 1556 cm^{-1}, identified as the symmetric and asymmetric stretching bands of the COO$^-$ group, similar to the corresponding peaks in the spectrum of sodium laurate.

A low-resolution SEM image of a top view (Figure 2 a) of the ZnAl-LDH–NO$_3^-$ film shows that the surface is microscopically relatively smooth. At higher resolution (Figure 2 b), it can be seen that the film is composed of curved hexagonal platelets lying perpendicular to the surface of the substrate; the thickness of the platelets was estimated to be on the order of 0.06–0.08 μm. This is comparable to the value of about 0.057 μm calculated by using the Scherrer equation based on the line width of the [003] reflection in the XRD pattern of the film (Figure 1 a). After treatment with laurate, the morphology of the film changes significantly. At the microscale, the surface becomes covered with hemispherical protrusions about 20–30 μm in diameter, with relatively smooth regions remaining in-between (Figure 2 c). Figures 2 d and e show higher magnification SEM images of a single hemispherical protrusion, which consists of LDH crystallites with hexagonal platelike morphology, oriented roughly perpendicular to the surface. The areas between the protrusions consist of a similar arrangement of hexagonal platelike crystallites (Figure 2 f). From Figure 2 e and f, it can be estimated that the thickness of the ZnAl-LDH–laurate platelets is 0.27–0.30 μm. This is similar to the value of about 0.24 μm calculated by using the Scherrer equation based on the line width of the [003] reflection in the XRD pattern of the film (Figure 1 b). The thickness of the platelets is approximately four times that of the ZnAl-LDH–NO$_3^-$ platelets (Figure 2 b). This is comparable to the increase in basal spacing (by a factor of 3.8) observed by XRD, associated with replacing nitrate by the much larger laurate anions.[17] Possibly, the expansion in crystallite thickness associated with intercalation of the laurate anions induces considerable stress in the film, which is relieved by the formation of the hemispherical protrusions.

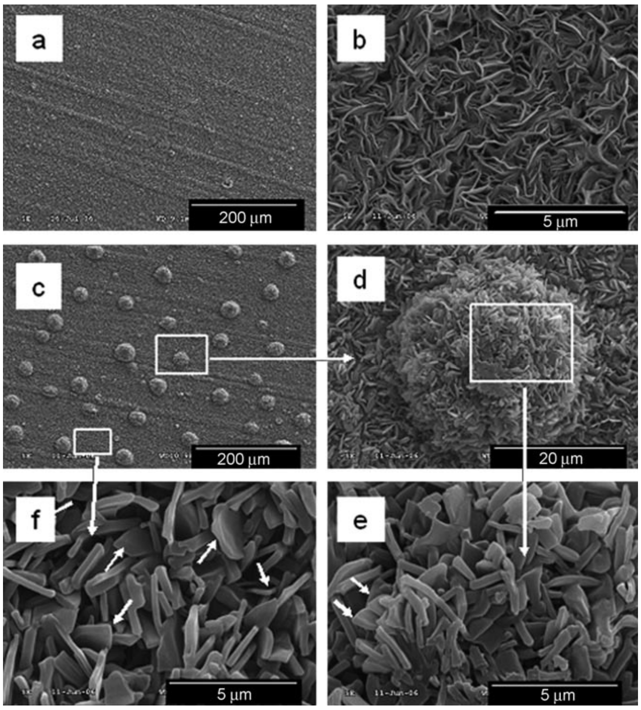

Figure 2. SEM images of a) the ZnAl-LDH–NO$_3^-$ film at low magnification, b) the ZnAl-LDH–NO$_3^-$ film at high magnification, c) the ZnAl-LDH–laurate hybrid film showing the hemispherical protrusions. d) High magnification image of a hemispherical protrusion. e,f) Higher magnification images of the surface of a hemispherical protrusion and the flat surface, respectively.

The morphology and roughness of both the hemispherical protrusions and the intervening "flat" surfaces of the ZnAl-LDH–laurate hybrid film were also characterized by AFM. The cross-sectional profile of a representative protrusion (Figure 3 a) reveals a distance between peak and base of the protrusion of about 4 μm and a diameter of about 20 μm. A large number of "triangular" islands of various sizes are clearly resolved on the surface of the protrusion. The rms roughness and the ratio[18] of true to projected surface area S/S_o of the protrusion displayed in Figure 3 a are 1.07 μm and 1.90, respectively. The 3D AFM image and cross-sectional profile of the surface of the ZnAl-LDH–laurate film between the protrusions are shown in Figure 3 b. The surface is composed of randomly distributed platelets of ZnAl-LDH–laurate with lateral sizes in the range of hundreds of nanometers to several micrometers. The rms roughness and S/S_o value obtained from the image of the flat surface are 0.25 μm and 2.90, respectively.

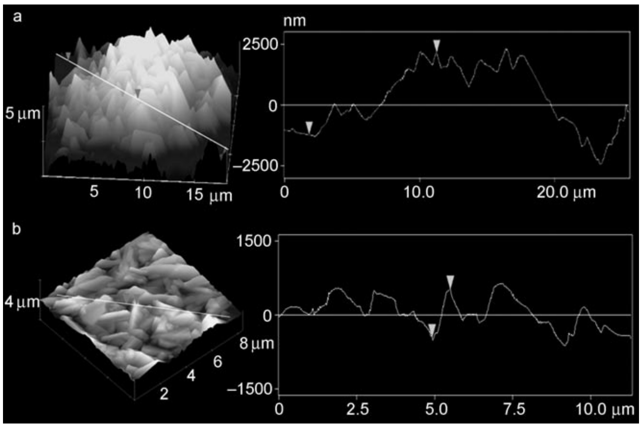

Figure 3. AFM images and corresponding cross-sectional roughness profiles of ZnAl-La-LDH hybrid film: a) for the hemispherical protrusions and b) for the regions between the protrusions.

The morphology of the ZnAl-LDH–laurate film involves both micro- and nanoscale hierarchical structures (the hemispherical protrusions and the edges of the crystallites, respectively) and can be said to resemble that of the lotus leaf, which involves microscale papillae covered with nanoscale wax hairs.[19] It can therefore be expected to show superhydrophobicity. The water contact angle of ZnAl-LDH–laurate hybrid film of about 163° is indeed in the superhydrophobic range.

The corrosion resistance of the LDH films was investigated by dc polarization;[8] the lower the polarization current, the better the corrosion resistance. Samples were immersed in a corrosive medium (3.5 % aqueous sodium chloride solution) for 30 min before the test. The polarization current of the PAO film (Figure 4b) is very similar to that of the untreated Al substrate (Figure 4a), that is, the oxide layer provides little additional corrosion resistance, consistent with its porous nature.[3,4] After coating the PAO layer with the ZnAl-LDH–NO_3^- film, the polarization current is reduced by two orders of magnitude (Figure 4c). A further large decrease in polarization current occurs when the PAO film is directly coated with laurate anions (Figure 4d) or when the ZnAl-LDH–NO_3^- film is treated with the same species (Figure 4e). Such low current densities as that measured for the ZnAl-LDH–laurate film (10^{-9} A cm^{-2}) have not been observed previously for layered coating materials or their powder counterparts.[5–9] Even after immersion in the corrosive medium for 21 d, the material coated with ZnAl-LDH–laurate still exhibited current densities as low as 10^{-8} A cm^{-2} (Figure 4f). The open-circuit potential was measured for the ZnAl-LDH–laurate film immersed in the corrosive medium; the value remained relatively stable in the range ± 0.10 V (vs SCE) up to an immersion time of 21 d, and thus the excellent corrosion resistant properties of the superhydrophobic coating were confirmed.

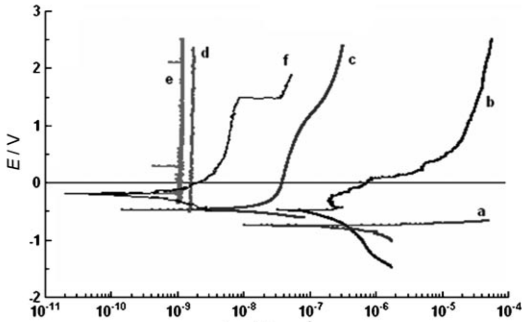

Figure 4. Polarization curves (vs SCE) of samples immersed in 3.5 % aqueous sodium chloride solution at room temperature for 30 min: a) bare Al substrate, b) PAO/Al substrate, c) ZnAl-LDH–NO_3^- film, d) PAO/Al–laurate film, and e) ZnAl-LDH–laurate film. f) ZnAl-LDH–laurate film after immersion for 21 d.

The SEM images of samples exposed to 3.5 % aqueous sodium chloride solution for different times at room temperature are shown in the Supporting Information. After 12 d, the bare Al substrate is clearly badly corroded and pitting corrosion can be observed on the PAO/Al surface. Some disfigurement occurs on the surface of the ZnAl-LDH–NO_3^- film and pinhole defects appear on the PAO/Al–laurate film. In contrast, the ZnAl-LDH–laurate film shows no apparent defects after immersion for 12 d, which is consistent with the polarization data discussed above. After immersion in the sodium chloride solution for a longer period of 21 d, the SEM micrographs indicate that the surface of the ZnAl-LDH–NO_3^- film is badly corroded, while more extensive pinholes appear on the PAO/Al–laurate film. However, the surface of the ZnAl-LDH–laurate film remains unchanged, and this confirms the superior barrier properties of the superhydrophobic film.

Although the water contact angle of the ZnAl-LDH–laurate film decreased from 163 to 140° on initial immersion in 3.5 % aqueous sodium chloride solution, the contact angle subsequently remained constant over a prolonged immersion period of 31 d. The XRD patterns of the fresh superhydrophobic ZnAl-LDH–laurate film and the same film after exposure to 3.5 % sodium chloride solution at room temperature for 31 d were also essentially identical. There is no evidence of intercalation of chloride ions from the medium or of carbonate ions by interaction with atmospheric carbon dioxide, as is often observed for LDHs.[11] This confirms that ZnAl-LDH–laurate films exhibit good stability during long-term immersion, and by virtue of retaining their structural integrity and hydrophobic properties they are able to provide long-term corrosion protection.

High coverage and adhesion of the coating are essential if the coating is to have effective anticorrosion properties. A cross-sectional SEM image of the ZnAl-LDH–laurate hybrid film (see the Supporting Information) shows the continuous nature of the polycrystalline LDH coating. The adhesion of the LDH–NO_3^- and LDH–laurate films to the aluminum substrate was analyzed according to the literature method.[8b] There was no significant peeling of either LDH layer after cross-cutting through the coating, that is, adhesion between the metal and both LDH coatings is strong.

Aluminum alloys containing small quantities of other metals such as Cu, Mg, and Fe are even more susceptible to corrosion than pure aluminum. X-ray diffraction, SEM, and water contact angle measurements (see the Supporting Information) confirmed that an analogous superhydrophobic LDH–laurate film can form on an aluminum alloy substrate (AA2024). The dc polarization measurements show that the LDH–laurate film coating gives current densities as low as 10^{-8} A cm^{-2} and thus provides an effective corrosion-resistant coating which is far superior to the hydrophilic LDH–NO_3^- film.

In conclusion, we have shown that anion exchange of laurate with a ZnAl-LDH–NO_3^- film on a PAO/Al substrate affords a ZnAl-LDH–laurate film with many microscale hemispherical protrusions on its surface; these protrusions are composed of nanoscale platelike ZnAl-LDH–laurate crystallites. The superhydrophobic properties of the film may result from the presence of both micro- and nanoscale hierarchical structures. The superhydrophobic nature of the film provides long-term corrosion protection of the coated aluminum substrate and provides an effective barrier to aggressive species. Self-healing properties of anticorrosion coatings are very important.[20] By taking advantage of the most attractive feature of LDH chemistry, that is the ability to modify the properties of the film by co-intercalation of other anions,[11] it should be possible to fabricate a superhydrophobic LDH coating with self-healing properties by co-intercalation of anions with a corrosion-inhibiting function which can be released in a controlled manner.[6a,20d] The preparation of the ZnAl-LDH–laurate film is simple, cheap, and amenable to scaleup, and it has potential for commercial application in the corrosion protection of aluminum.

Experimental Section

Fabrication of ZnAl-LDH–NO_3^- films: A porous anodic alumina/aluminum (PAO/Al) substrate was fabricated by anodizing aluminum metal sheet (Shanghai Jing Xi Chemical Technology Co., Ltd, purity: > 99.5 %, thickness: 0.1 mm) in a thermostatic bath of 1 M H_2SO_4 at ambient temperature and a current density of 20 mA cm^{-2} for 50 min.[12] $Zn(NO_3)_2\cdot 6H_2O$ (0.01 mol) and NH_4NO_3 (0.06 mol) were dissolved in deionized water (100 mL), and 1 % ammonia solution was then slowly added until the pH reached 6.5. The PAO/Al substrates were then placed in the above solution in a water bath at 45 °C for 36 h. Finally, the substrates were removed, rinsed with ethanol, and dried at room temperature.

Synthesis of ZnAl-LDH–laurate hybrid films: The ZnAl-LDH–NO_3^- film was immersed in a 0.05 M aqueous solution of sodium laurate at 50 °C for 7 h. The resulting film was rinsed with ethanol and then dried at room temperature.

Powder XRD data were collected on a Rigaku XRD-6000 powder diffractometer with $Cu_{K\alpha}$ radiation (40 kV, 30 mA, λ = 1.542 Å). Scanning electron microscopy (SEM) was carried out on a Hitachi S-3500N instrument, and scanning probe microscopy on a Nanoscope IIIa MultiMode SPM (Veeco Instruments, Santa Barbara, CA) in tapping mode under ambient conditions. Roughness data were obtained by using the atomic force microscopy (AFM) software (Digital Instruments, Version 6.12). Polarization curves were obtained by using a Cypress Systems CS-300 potentiostat at room temperature. A three-electrode configuration was employed in the circuit with the sample as working electrode, a platinum counter-electrode, and a saturated calomel electrode as reference electrode. An 3.5 % aqueous solution of sodium chloride was used as electrolyte. The sweep rate was set at 10 mV s^{-1}. Static water contact angles were measured with a commercial system for drop-shape analysis (DSA 100, Krüss GmbH, Germany) at ambient temperature. The equilibrium water contact angle was measured with a fixed needle supplying a water drop while the drop-shape analysis system determined the contact angle. Three different points on each sample were investigated, and the average value determined.

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[1] R. C. Newman, K. Sieradzki, *Science* **1994**, *263*, 1708.

[2] a) D. Chidambaram, C. R. Clayton, G. P. Halada, *J. Electrochem. Soc.* **2004**, *151*, B151; b) J. Zhao, G. S. Frankel, R. L. McCreery, *J. Electrochem. Soc.* **1998**, *145*, 2258; c) L. Xia, R. L. McCreery, *J. Electrochem. Soc.* **1998**, *145*, 3083; d) D. Chidambaram, C. R. Clayton, G. P. Halada, *Electrochim. Acta* **2006**, *51*, 2862.

[3] a) A. Kuznetsova, T. D. Burleigh, V. Zhukov, J. Blachere, J. T. Yates, *Langmuir* **1998**, *14*, 2502; b) R. C. Barik, J. A. Wharton, R. J. K. Wood, K. R. Stokes, R. L. Jones, *Surf. Coat. Technol.* **2005**, *199*, 158; c) X. Li, X. Nie, L. Wang, D. O. Northwood, *Surf. Coat. Technol.* **2005**, *200*, 1994.

[4] S. G. Xin, L. X. Song, R. G. Zhao, X. F. Hu, *Thin Solid Films* **2006**, *515*, 326.

[5] a) G. Williams, H. N. McMurray, *Electrochem. Solid-State Lett.* **2003**, *6*, B9; b) G. Williams, H. N. McMurray, *Electrochem. Solid-State Lett.* **2004**, *7*, B13.

[6] a) R. G. Buchheit, H. Guan, S. Mahajanam, F. Wong, *Prog. Org. Coat.* **2003**, *47*, 174; b) R. G. Buchheit, S. B. Mamidipally, P. Schmutz, H. Guan, *Corrosion* **2002**, *58*, 3; c) W. Zhang, R. G. Buchheit, *Corrosion* **2002**, *58*, 591.

[7] a) J. M. Yeh, C. L. Chen, Y. C. Chen, C. Y. Ma, K. R. Lee, Y. Wei, S. Li, *Polymer* **2002**, *43*, 2729; b) J. M. Yeh, S. J. Liou, C. Y. Lai, P. C. Wu, T. Y. Tsai, *Chem. Mater.* **2001**, *13*, 1131.

[8] a) A. Mitra, Z. B. Wang, T. G. Cao, H. T. Wang, L. M. Huang, Y. S. Yan, *J. Electrochem. Soc.* **2002**, *149*, B472; b) D. E. Beving, A. M. P. McDonnell, W. S. Yang, Y. S. Yan, *J. Electrochem. Soc.* **2006**, *153*, B325; c) X. L. Cheng, Z. B. Wang, Y. S. Yan, *Electrochem. Solid-State Lett.* **2001**, *4*, B23.

[9] J. K. Choi, Z. P. Lai, S. Ghosh, D. K. Beving, Y. S. Yan, M. Tsapatsis, *Ind. Eng. Chem. Res.* **2007**, *46*, 7096.

[10] a) L. N. Mitchon, J. M. White, *Langmuir* **2006**, *22*, 6549; b) G. Hähner, R. Hofer, I. Klingenfuss, *Langmuir* **2001**, *17*, 7047; c) H. Gao, N. N. Gosvami, J. Deng, L. Tan, M. S. Sander, *Langmuir* **2006**, *22*, 8078; d) P. E. Hintze, L. M. Calle, *Electrochim. Acta* **2006**, *51*, 1761; e) I. L. Liakos, R. C. Newman, E. McAlpine, M. R. Alexander, *Langmuir* **2007**, *23*, 995.

[11] a) D. G. Evans, X. Duan, *Chem. Commun.* **2006**, 485; b) G. R. Williams, D. O'Hare, *J. Mater. Chem.* **2006**, *16*, 3065; c) D. G. Evans, R. C. T. Slade, *Struct. Bonding (Berlin)* **2006**, *119*, 1; d) J. He, M. Wei, B. Li, Y. Kang, D. G. Evans, X. Duan, *Struct. Bonding (Berlin)* **2006**, *119*, 89.

[12] H. Y. Chen, F. Z. Zhang, S. S. Fu, X. Duan, *Adv. Mater.* **2006**, *18*, 3089.

[13] L. Vayssieres, N. Beermann, S. E. Lindquist, A. Hagfeldt, *Chem. Mater.* **2001**, *13*, 233.

[14] A. Legrouri, M. Badreddine, A. Barroug, A. D. Roy, J. P. Besse, *J. Mater. Sci. Lett.* **1999**, *18*, 1077.

[15] a) M. Borja, P. K. Dutta, *J. Phys. Chem.* **1992**, *96*, 5434; b) T. Kanoh, T. Shichi, K. Takagi, *Chem. Lett.* **1999**, 117.

[16] Z. P. Xu, P. S. Braterman, K. Yu, H. Xu, Y. Wang, C. J. Brinker, *Chem. Mater.* **2004**, *16*, 2750.

[17] J. H. Lee, S. W. Rhee, D. Y. Jung, *Chem. Commun.* **2003**, 2740.

[18] H. M. Shang, Y. Wang, S. L. Limmer, T. P. Chou, K. Takahashi, C. Z. Cao, *Thin Solid Films* **2005**, *472*, 37.

[19] X. Feng, L. Jiang, *Adv. Mater.* **2006**, *18*, 3063.

[20] a) D. G. Shchukin, M. Zheludkevich, K. Yasakau, S. Lamaka, M. G. S. Ferreira, H. Möhwald, *Adv. Mater.* **2006**, *18*, 1672; b) M. L. Zheludkevich, D. G. Shchukin, K. A. Yasakau, H. Möhwald, M. G. S. Ferreira, *Chem. Mater.* **2007**, *19*, 402; c) M. W. Keller, S. R. White, N. R. Sottos, *Adv. Funct. Mater.* **2007**, *17*, 2399; d) H. Tatematsu, T. Sasaki, *Cem. Concr. Compos.* **2003**, *25*, 123.