

of the microcapsules from  $\sim 4.5 \mu\text{m}$  to  $\sim 3 \mu\text{m}$  and significantly increases the structural integrity of the capsules, which is attributed to the increase in wall thickness that accompanies the shrinking. They verified the structural integrity of the thermally-treated microcapsules by noting the percentage of capsules that were not deformed upon ingestion by cells; the capsules with thicker walls are reinforced and thus are more suited to the delivery of encapsulated materials.

Using optical transmission microscopy, the researchers demonstrated the activation of a microcapsule inside a cancer cell using a laser with a wavelength of 830 nm and an incident intensity of 50 mW. The capsules had silver nanoparticles (diameter  $> 20 \text{ nm}$ ) embedded in the walls, but had no encapsulated material. Silver nanoparticles were chosen in part because they absorb the 830 nm light and in part because they provide dark contrast in the optical transmission microscope. The researchers also performed release experiments on AF-488 dextran encapsulated microcapsules that had gold or gold sulfide nanoparticles embedded in the walls. These studies showed that ingested living cells adhere to the substrate both before and after the release of the encapsulated polymer, demonstrating that this method is feasible for the delivery of materials into specific cells. The studies also showed that microcapsules that were merely adhered to the outer membrane were lifted up and away from the cells during illumination and were not disrupted, demonstrating that only the ingested microcapsules release their encapsulated material upon irradiation.

THAD AWEKA

### Pitting Sites on Al Controlled by Microcontact Printing Using Poly(chloroprene) Rubber Mask Film

The arrangement of uniform tunnel pits at regular intervals is essential to maximize the surface area of Al electrodes for electrolytic capacitors. However, tunnel pits obtained by conventional anodic etching are not regularly distributed on an Al foil. Recently, K. Nishio and colleagues at Tokyo Metropolitan University developed a method to precisely control the initiation sites of tunnel pits on Al.

As described in their article in the September issue of *Electrochemical and Solid-State Letters* (p. B39; DOI: 10.1149/1.2214364), the researchers used poly(chloroprene) rubber (CR) as a masking material for the elastomeric stamp to control the pitting sites on Al. The researchers first cast a prepolymer of poly(dimethyl-

siloxane) (PDMS) on a metal mold with an ideally ordered array of convex protrusions on its surface and cured it for 12 h at room temperature. After they mechanically detached the PDMS hole array (stamp) from the metal mold, the researchers dipped the stamp in a 1 wt% toluene solution of CR and pulled it at a constant rate. When the toluene evaporated, a thin CR film was formed on the stamp. They then transferred the CR film on the stamp to an Al foil through physical contact and detachment since the adhesion of CR to Al is much stronger than to PDMS. They then etched the Al foil covered with the patterned CR film in HCl solution under a constant dc current condition. The CR film printed on the Al foil masks against the anodic etching of the Al so that no pits are initiated on the CR film. Using this method, the researchers fabricated uniform pits arranged in an ideal array over the Al film with the same  $\langle 100 \rangle$  orientation, a width of  $\sim 3 \mu\text{m}$ , a depth of  $\sim 1.5 \mu\text{m}$ , and an interval of  $5.0 \mu\text{m}$ . While the width and interval of the pits can be precisely controlled, the researchers could not control the depth of the pits, because prolonged etching induces a substantial dissolution of the sidewalls of the pits. Further study is needed to make the pits sufficiently deep.

The researchers said that using this process, they can optimize the surface area of an Al electrode for electrolytic capacitors by forming ordered arrays of fine and deep tunnel pits. They also said that their technique can be applied in other electrochemical and photoelectrochemical etching of semiconductors such as Si, InP, GaAs, and GaN for simple site control of pitting.

TAO XU

### Sol-Gel Hybrid Film with Benzotriazole-Doped $\text{SiO}_2$ Nanoreservoirs Provides Corrosion Protection to Al Alloy by Controlled Release of Inhibitor

Thin sol-gel films containing inhibitors have emerged as a potential adhesive for polymer-based coating systems with self-healing capabilities, but the integrity of the film is affected unless the inhibitor is isolated from the matrix. The concept developed to overcome this problem is based on placing the inhibitor in a reservoir or container that would slowly release it as corrosion is initiated. The addition of nanometer-sized reservoirs ensures a homogeneous distribution of corrosion protection along the film.

Using a layer-by-layer technique to fabricate reservoirs, D.G. Shchukin of the Max Planck Institute of Colloids and Interfaces in Germany; M. Zheludkevich of the

University of Aveiro, Portugal; and their colleagues created a hybrid  $\text{ZrO}_2/\text{SiO}_2$  sol-gel film in which  $\text{SiO}_2$  nanoparticles coated with polyelectrolyte layers act as nanoreservoirs of the inhibitor benzotriazole, protecting an aluminum AA2024 alloy from corrosion. The layer-by-layer technique consists of depositing layers of solutions with opposite charge, leading to a multilayer assembly in which permeability can vary depending on the nature of the solutions involved. The researchers said that if polyelectrolytes are used as a shield for the inhibitor, the fact that its permeability changes with pH and humidity would allow controlled release of the inhibitor, depending on the very variables that determine corrosion initiation.

As explained in the July issue of *Advanced Materials* (p. 1672; DOI:10.1002/adma.200502053), the research team, led by H. Möhwald of MPI, deposited positively charged polyethyleneimine (PEI) on the negatively charged  $\text{SiO}_2$  nanoparticles, with subsequent layers of polystyrene sulfonate (PSS) and benzotriazole, resulting in a multilayer structure of the form PEI/PSS/inhibitor/PSS/inhibitor. In order to evaluate the corrosion-protection abilities of the nanoreservoir-doped film, the researchers compared its performance in a NaCl aqueous solution with an undoped  $\text{ZrO}_2/\text{SiO}_2$  film and a film containing freely added benzotriazole (0.13 wt% and 0.63 wt%). Impedance measurements along a range of frequencies revealed some corrosion activity occurring in both films with free inhibitor, showing a decrease of one order of magnitude in the resistance of the film containing 0.13 wt% benzotriazole, and two orders of magnitude for the one containing 0.65 wt% benzotriazole, when compared with the undoped film. Other signs of structural degradation were found when evaluating capacitance: after 20 h in the corrosive environment, the undoped film capacitance increased by one order of magnitude while the 0.13 wt% free-inhibitor film increased by four orders of magnitude, highlighting the damaging effect of the free inhibitor in the film.

At this point, the undoped and nanoreservoir-doped films had demonstrated similar corrosion resistance in a 48 h period. The added benefit of the nanoreservoirs was then confirmed after the investigators introduced an identical defect on each film. Local measurements of corrosion activity using the scanning vibrating electrode technique revealed in both cases an initial severe drop in resistance, with the undoped film showing a continuous decrease in a slower ramp. For the doped film, the severe initial drop was