

Smart Nanoparticles Serve in Corrosion-Inhibiting Coatings

Surface-modified nanoparticles are an ideal platform for “smart” corrosion-inhibiting additives because their high surface areas allow them to act as carriers and reservoirs of organic corrosion inhibitors. Organic corrosion inhibitors, often highly effective in preventing corrosion, have functional groups that are reactive with coatings resins, thereby locking the corrosion inhibitor into the coating and preventing it from migrating to the corrosion site. Attaching them to a nanoparticle provides a means for protecting the corrosion inhibitors until needed. In addition, the surface chemistry of nanomaterials is often different from that of the same materials in the bulk phase, thus allowing for novel release mechanisms to be developed. A smart nanoparticle-based additive that releases organic corrosion inhibitors when triggered by atmospheric corrosion has been developed by TDA Research Inc.

Using an agglomerated commercial aluminum oxyhydroxide (AlOOH, boehmite) as a starting material, the company has developed chemical methods to reduce the agglomerates to nano-sized (~40 nm × 40 nm × 2.5 nm) primary crystallites. Their surfaces are then built up with covalently bonded corrosion inhibitors and secondary groups that provide dispersion of the nanoparticle carriers in the coating resins. The resulting surface-modified boehmite nanoparticles have been incorporated into several commercial epoxy resins. They have shown good corrosion protection on aluminum alloys, matching the protection provided by chromated epoxy resins.

Most high-strength aluminum alloys, such as those used for the airframes of modern aircraft, use copper as an alloying agent. The most common alloys used are Al-2024 (an aluminum/copper alloy) and Al-7075 (an aluminum/zinc/copper alloy). The compounding of aluminum and the alloying element(s) causes the alloy's susceptibility to corrosion. Corrosion of Al/Cu alloys (as with other metals) proceeds when there are continuous electrical and ionic contacts between the anode and cath-

ode and also an ambient cathodic reactant such as O₂, H₂O, or H₂.

In Al/Cu alloys, the reaction O₂ + 2H₂O + 4e⁻ → 4OH⁻ (neutral/alkaline conditions) is promoted on the Cu sites contained within or formed on the aluminum alloy surface. TDA Research has used the generation of alkaline conditions at the copper sites to trigger the release of the organic corrosion inhibitors.

Soluble chromates are the most effective and most widely used corrosion inhibitors for high-strength aluminum alloys. Chromates are added to protective organic coatings because the coating alone is not sufficient to protect the underlying metal substrate from corrosion. Even the best organic coatings contain micropores, areas of low cross-link density, or high pigment volume concentrations (PVCs), that provide a diffusion path to the metal surface for corrosive agents such as water, oxygen, and chloride ions. However, the use of chromates and other chromium-containing compounds has become more restricted since 1982 because of their toxicity.

The ideal corrosion-inhibiting additive would hold nontoxic, highly effective corrosion inhibitors in a non-leachable form until the onset of corrosion of the metal released the corrosion inhibitor; the corrosion inhibitor should be released only when needed. TDA Research has based the design of their corrosion-inhibiting nanoparticles on a pH-triggered release. Organic corrosion inhibitors attached to the nanoparticles are released when the

pH rises above ~9. This occurs in atmospheric corrosion when the reduction of oxygen in the presence of water produces hydroxide ions.

Recent modeling studies have found that pH dependence of the inhibitor release is a critical factor in optimizing the effectiveness and service life of a corrosion-inhibiting coating. Triggered release prevents premature depletion of the inhibitor reservoir of the coating and a pH-dependent release mechanism provides a sharp turn-on/turn-off release mechanism. In the TDA approach, the triggered release of organic corrosion inhibitors is dependent on the presence of a labile bond that can be disrupted by products (OH⁻) released by the corrosion process.

Three independent tests of these corrosion-inhibiting nanoparticle additives have been carried out using resins from three major paint manufacturers. In each case, the corrosion-inhibiting nanoparticle additives equaled or exceeded the performance of chromated epoxy controls in a salt fog test (ASTM B-117) and in filiform corrosion tests on Al-2024 alloys. Filiform corrosion is a thread-like form of corrosion that occurs primarily under organic coatings on aluminum alloys. The source of initiation is usually a defect or mechanical scratch in the coating. The test for filiform corrosion is to place a concentrated acid such as HCl into a scribe on a coated panel, process the panel through wet and dry cycles for 1000 h, and evaluate filiform corrosion as it grows away from the scribe under the organic coating.

Opportunities

TDA Research Inc. is interested in working with coating manufacturers and additive suppliers to incorporate its patented nanoparticle-based corrosion-inhibiting additives into coatings for use on aluminum, steel, copper, magnesium, brass, and titanium.

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Multilayer Thin-Film Coatings Protect Sensitive Electronics from Atmospheric Exposure

Recent developments in thin-film electronics, such as organic light-emitting devices (OLEDs), organic transistors, photovoltaics, and batteries, have made possible bendable electronic devices. Flexible OLED displays have been fabricated on thin plastic and metal foil substrates. However, commercialization of flexible OLEDs is hindered by their high sensitivity to moisture. Both hydrolysis and oxidation of the thin electrodes produce non-emissive regions in the display that can lead to failure. Therefore, hermetic sealing (encapsulation) of the OLED is required to achieve acceptable lifetimes. Unfortunately, the best thin-film encapsulation methods have water vapor transmission rates (WVTRs) that are orders of magnitude higher than those needed for successful OLED encapsulation. Similar encapsulation is also required for other thin-film electronic components. Scientists at Pacific Northwest National Laboratory (PNNL) have developed a multilayer thin-film deposition process and structure that achieves the rigorous encapsulation requirements for OLEDs while retaining flexibility, thereby enabling long-lived, bendable, flat-panel displays. In addition to OLED displays, the PNNL multilayer encapsulation method has been demonstrated with thin-film solar cells and lithium batteries.

Encapsulation of OLEDs requires a gas diffusion barrier with a WVTR below 10^{-6} g/m²/day (25°C/40% RH). After optimization, the best vacuum-deposited inorganic thin films only attain WVTR values of 10^{-4} – 10^{-3} g/m²/day, due to the existence of micro- and/or nanometer-sized defects in the extremely thin layers. Deposition of multiple inorganic layers does not remedy the problem, since the atomistic vacuum-deposition processes tend to extend defects from the previous layer. Multilayer alternating laminates of organic and inorganic structures provide an architecture in which defects in adjacent inorganic layers

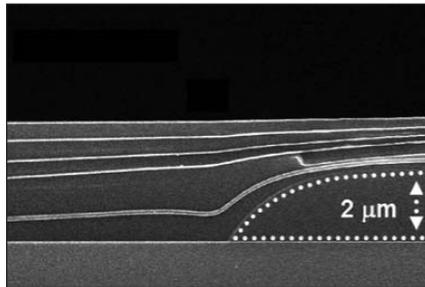


Figure 1. Scanning electron micrograph cross section of a typical multilayer organic-inorganic barrier stack deposited over a $\sim 2 \mu\text{m}$ structure. The thin ($\sim 40 \text{ nm}$), lighter-colored layers are inorganic aluminum oxide, and the darker layers are organic (acrylate) polymers. The air interface is at the top.

can be effectively decoupled.

A cross section of a multilayer barrier film deposited over a segmented OLED pixel is shown in Figure 1. The encapsulation structure contains a combination of organic and inorganic thin-film layers with a total stack thickness of $\sim 5 \mu\text{m}$. The vacuum-deposited inorganic films are the primary barrier to gas permeation and must be as defect-free as possible. This requires the use of high-energy deposition methods such as plasma-enhanced chemical vapor deposition or magnetron sputtering.

The organic layers have several functions. First, the thicker organic (polymeric) layers “level” surface asperities or debris and provide a high quality surface for subsequent deposition of the nanometer scale ($<50 \text{ nm}$) inorganic layers. This helps prevent structural compromise, such as flaws or breaks, in the fragile inorganic layers. Second, by separating adjacent inorganic layers, the multilayer design creates an extremely long diffusion path for gas molecules.

High-quality, vacuum-deposited, inorganic thin films contain small ($<1 \mu\text{m}$) defects that are spaced tens to hundreds of micrometers apart. When multiple inor-

ganic layers are separated by organic interlayers, large spacing between defects in the inorganic layers produces a long diffusion path in the organic interlayer. This condition is repeated multiple times in a three- to five-pair film—resulting in a long, tortuous path for diffusing species and a pronounced increase in lag time as the diffusion front advances through the multiple layers. Lag times in excess of one year have been measured on encapsulated thin-film calcium test structures.

Encapsulated OLED test pixels show no change in the luminance, current, and voltage characteristics after $>1160 \text{ h}$ of accelerated testing at 60°C and 90% RH. In addition, the efficiency of copper indium diselenide solar cells was unchanged after 1000 h of accelerated testing (60°C and 90% RH) when encapsulated using the multilayer barrier coatings, while unencapsulated cells degraded rapidly under identical conditions. The multilayer thin-film architecture makes optimum use of both transient (lag time) and steady-state (WVTR) diffusion regimes to achieve the required barrier performance.

The ultra-barrier thin-film structures are deposited at low temperatures ($<80^\circ\text{C}$), allowing direct application of the coating over fragile electronic devices. In addition, the barrier layers can be deposited using either continuous roll-to-roll or batch manufacturing methods.

Opportunities

The PNNL multilayer barrier technology, which can be used to hermetically seal fragile thin-film devices from atmospheric degradation and facilitate long-lived flexible OLED displays, is available for collaborative research and licensing.

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