# Skin with high rust protection factor

June 4 2014, by Peter Hergersberg

Credit: AI-generated image (disclaimer)

In industrialized countries, corrosion guzzles up to 4 percent of economic performance annually. Substances that protect metals effectively from its ravages are often damaging to the environment or have other disadvantages. Consequently, scientists working with Martin Stratmann and Michael Rohwerderat the Max-Planck-Institut für Eisenforschung (Iron Research) in Düsseldorf are developing synthetic coatings that can protect steels and other metals from rust and heal themselves if they become damaged.

Erin Brockovich made the world conversant with a problem that researchers at the Max-Planck-Institut für Eisenforschung now hope to solve once and for all. Brockovich's story is one of poison, big money and the health of almost 2,000 people; and it is the story of a woman who did a great deal to bring a powerful corporation to its knees. These ingredients provided just the kind of mix that Hollywood likes to work with. The fact that the film Erin Brockovich stars Julia Roberts as the eponymous American legal clerk and environmental activist probably created a greater awareness of the problem: the carcinogenic chromium(VI).

Between 1952 and 1966, the California energy firm Pacific Gas and Electric Company allowed the substance to seep into the groundwater of the town of Hinkley. As a result, following the legal proceedings brought by Erin Brockovich, the corporation was required to pay some 200 million dollars to the inhabitants of the town, and another 133 million dollars to the lawyers.

Chromium(VI) salts are still the standard in corrosion protection, but have since been banned from use in many other applications. The search is now on for an equally effective, but environmentally sound alternative. After all, industrialized countries see 3 to 4 percent of their gross domestic product eaten away by corrosion each year; in Germany alone, this represents more than 75 billion euros. Martin Stratmann and Michael Rohwerder at the Max-Planck-Institut für Eisenforschung in Düsseldorf are studying the corrosion process, which affects primarily metal materials, and searching for ways to prevent it.

Their aim is to identify synthetic coatings that will protect various metals, but especially steel and aluminum, from corrosion, and that will heal themselves when damaged, just like the skin of living beings. Such a coating – normally underneath a colored lacquer – would constitute a bulwark against metal-guzzling rust. In most steels, a zinc coating applied directly to the sheet forms an additional barrier; in the case of aluminum, this takes the form of a dense and highly resistant oxide layer. In the event that the protective layers and even the metal underneath are damaged by scratching, it is intended that the synthetic coating will hold off any corrosion, possibly with the help of the zinc, until the gash in the material is sealed off again.

## Benefits in two fields: finish first, then fabricate

Not only would this kind of overlay eliminate the problem of chromium(VI), but it could also boast other advantages. It should enable steel manufacturers, for example, to reduce at least the zinc layer, as even zinc is controversial in some ways. "The zinc coating can actually heal itself to a certain extent, because it also deposits passivating zinc oxide in gashes and holes, preventing further corrosion," says Michael Rohwerder, head of the Molecular Structures and Surface Design Research Group. "However, it is considered problematic from an environmental perspective, and it is expensive and vaporizes easily during laser welding, contaminating the welding equipment."

Coatings such as those being developed by the materials scientists in Düsseldorf could also minimize maintenance requirements for aircraft. Any fine scratches on their wings, for example, would be sealed off immediately by a self-healing layer. As things stand today, airlines must regularly comb their aircraft for even the slightest damage, only to repair it at considerable expense.

Finally, the self-healing skin for metals could mark a new chapter in car and machinery manufacture. Currently, car bodies can't be treated with protective coatings until they have their final shape. It would be cheaper to treat the steel beforehand, but would do little good, as fine cracks form in the protective skin while the material is being formed. Again, a self-healing layer could solve this problem, benefitting car manufacturers and mechanical engineers, as well as steel producers. The manufacturers could cut out an expensive step that has nothing to do with their core business, while steel producers could make their products more valuable and lucrative.

Martin Stratmann and Michael Rohwerder thus have no shortage of reasons for developing self-healing polymer coatings – however, it is a task that poses many challenges. In order to understand where the difficulties lie and what tricks the Düsseldorf-based scientists have used (or plan to use) to overcome them, it is helpful to take a quick look at the corrosion process.

"Corrosion is the reversal of metallurgy," says Martin Stratmann, Director of the Interface Chemistry and Surface Engineering Department of Düsseldorf's Max Planck Institute. It can affect all metals except precious metals. Rust is probably the most prominent and economically relevant case, occurring when oxygen oxidizes iron. Iron corrosion destroys the work of the furnace, which transforms iron oxides and other ores into elementary metals.

## Ions whet the appetite of oxygen

In completely dry air, iron wouldn't corrode. Atmospheric oxygen under these conditions would be only too happy to gnaw away at the metal. But in the absence of moisture, the iron is quickly put out of its reach, similar to a can of feed closing while a dog was eating from it. This is because a thin layer of iron oxide forms quickly on iron that is exposed to air, and in dry conditions, oxygen isn't reactive enough to penetrate this layer.

Once water, or in the worst case saltwater, comes into play, however, the situation is entirely different. For one thing, a porous, moist mixture of different oxides forms on the iron, and these crumble off in layers, serving up a constant supply of food for the oxygen. In addition, water – and above all saltwater – contains ions that act as appetizers and digestion enhancers for the rust, because they enable the oxygen present in the water to gain access to the metal. One way to measure a metal's susceptibility to corrosion is to find its electrochemical potential. The lower the potential, the more base the metal is, and the more easily it can fall prey to oxygen or another oxidizing agent.

But iron isn't the only material that covers itself with a protective layer at the first sign of oxygen attack; other metals, such as zinc, do the same. In the case of zinc, a very thick covering of zinc oxide and zinc carbonate forms on the surface, making it even more resistant at normal humidity than the more noble iron. The rust protection of galvanized sheet metal is based on this phenomenon, but not on this alone. Since zinc is more basic than iron, it corrodes first if the sheet is scratched. On the small exposed surface of the 7 micrometer thick zinc coating that has been damaged, the oxide is unable to form the structure it uses to keep the zinc from being guzzled from the side. At worst, it sacrifices itself entirely in order to protect the underlying steel from corrosion.

The team in Düsseldorf hopes to spare this sacrifice by using a polymer skin that can heal itself more comprehensively than zinc. They are building on their research into certain plastics that materials scientists working in the field of corrosion protection have been experimenting with for almost 30 years: conductive polymers. "These materials were used commercially for corrosion protection at an early stage, but they didn't work properly and most products have disappeared from the market," says Michael Rohwerder. "In some cases, using these products even led to increased corrosion." The Düsseldorf-based materials scientists have contributed much to the understanding of how conductive polymers prevent rust – when they do so – and why and under which conditions they fail.

A look under the skin: Ashokanand Vimalanandan adjusts the Kelvin probe that enables him to monitor whether a given polymer coating gives corrosion protection and self-heals when damaged. A fine needle acts as the Kelvin probe's electrode, positioned above the sample. The dark layer is the self-healing skin. Underneath the drop is a defect in which corrosion is starting. Credit: Frank Vinken

## Kelvin probe shows when corrosion begins

Martin Stratmann has developed an effective instrument for this task. Or more precisely: he had the idea of using a well-known device precisely for this purpose – the Kelvin probe. With its glass front, the box-shaped device is reminiscent of a microwave oven and approximately the same height. Inside it is a needle-shaped electrode, the centerpiece of the apparatus. This is used to measure voltage and determine how much effort must be expended in order to catapult electrons from a surface. This electron affinity is a measure of the chemical properties of a metal: it is smaller for base metals and relatively large in the case of noble metals. It also changes when there are changes in the surface of the material, such as when the metal begins to corrode. In these cases, the Kelvin probe records a drastic drop in voltage, whereas conversely, the voltage shoots upward as soon as the corrosion protection kicks in.

## Conductive polymers only protect against small defects

"The advantage of the Kelvin probe is that we can use it to follow the processes that occur at the surface of the metal through a film of moisture," says Martin Stratmann. The probe's glance penetrates more than just drops of water, however. "At some stage, without any major expectations, we just took a look at the metal through the polymer," explains the chemist. With that, the researchers landed a hit in a blind spot of materials science, because the Kelvin probe also yields reliable information when rust is eating steel underneath a polymer coating.

Using this tool, the researchers systematically screen different coatings that contain conductive polymers, and test their corrosion protection under changing conditions. The polymers consist of a positively charged structure that transports the current and mobile negative ions. According to the findings of the Max Planck research team, their protective effect arises because their electrochemical potential is higher than that of iron, for example, and they share an electrically conductive connection with it. As a result, they function not just as a barrier, like every other synthetic coating, but actually provide active protection for the metal. If the coating becomes damaged, the metal's lower potential adjusts to the polymer's potential, which is too high for corrosion to touch – at least in theory.

In practice, this protection is effective only if the damage isn't too extensive. There is no reprieve for the metal if scratches are wider than one tenth of a millimeter, and in most applications, protection that covers only damage of less than half a square millimeter in area isn't worth all that much. In addition, the polymer fails to live up to expectations when exposed to solutions containing chloride, as they are particularly aggressive promoters of corrosion. This is inconvenient if the coatings are intended to protect ships and cars from rust, given the rich chloride content of seawater and the salting of roads in winter.

## Active polymer coating may prevent protection sabotage

The polymer coatings provide better protection if they contain phosphate or similar anions in the form of mobile particles. Together with the ions from the corroding metal, they can form an overlay that shields the material from further attacks by oxygen and its hired helpers, in a similar way to zinc oxide and its mother metal. This can happen only if the anions are released when a corrosive attack occurs. In theory, this is possible, because in these conditions, the polymer structure snaps up the iron electrons that the oxygen is after, losing its charge and conductivity.

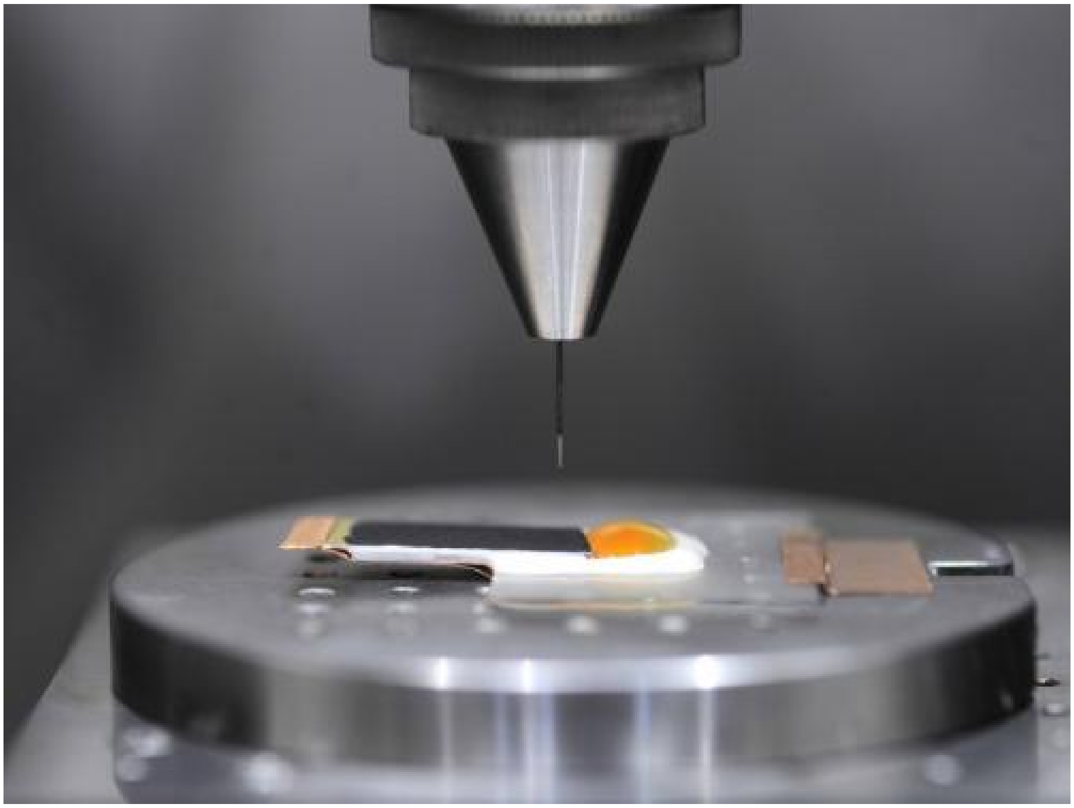
The negative counterions now need another charge equalization, which they find in the positive ions of the corroding metal. If all goes well, they migrate from the polymer coating into the scratches and, in the case of steel, form the desired protective layer with zinc or iron ions. All too often, however, all does not go well. "Then the metal ions flow into the polymer as on a freeway, actually accelerating corrosion," explains Michael Rohwerder.

So much for the rather patchy situation regarding corrosion protection using plastic skins. But there's also good news. The Düsseldorf-based Max Planck researchers' work is revealing ways to achieve corrosion protection that is less picky about when it will work, and, above all, never plays into the hands of the opponent.

The first clue came with the observation that the conductive polymers sabotage corrosion protection only when they form a continuous coating on the metal. However, if scientists distribute small clusters of ionic polymers in an electrically insulating plastic like cherries in a cake, the conductive polymers can leverage their strengths without acting as a highway to corrosion. "For corrosion protection to work, we have to make sure that the polymer particles are in contact with the underlying metal and at the right distance from each other," says Rohwerder.

From this discovery, it isn't that big a jump to the idea of integrating capsules in a non-conductive coating, such as the polyurethane used in paints and varnishes, which would release the components of the polyurethane overlay in case of damage, repairing the plastic coating in a more lasting way than zinc. The Hai Tran and Ashokanand Vimalanandan, two doctoral students in Michael Rohwerder's group, are working on this concept. The goal is that the coatings from their laboratory should heal cracks and scratches of over a tenth of a millimeter in width.

"In order to achieve this goal, we have to equip the self-healing layer with three properties," explains The Hai Tran. "First, it should allow the materials necessary for self-healing to escape when corrosion occurs." The substances should remain stable until an attack occurs, "but when they are needed, the capsules must release them without fail," adds Ashokanand Vimalanandan, "because a sufficient volume must flow into the defect so that it will be sealed off with a closed layer."

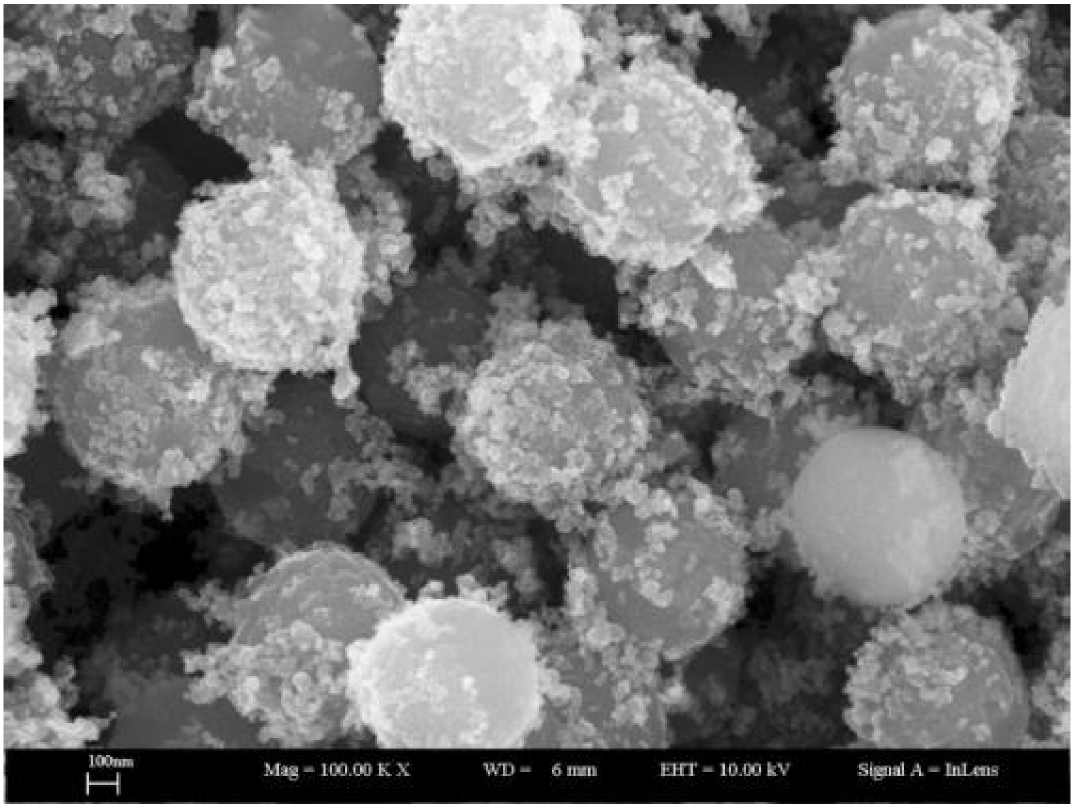


A look under the skin: Ashokanand Vimalanandan adjusts the Kelvin probe that enables him to monitor whether a given polymer coating gives corrosion protection and self-heals when damaged. A fine needle acts as the Kelvin probe's electrode, positioned above the sample. The dark layer is the self-healing skin. Underneath the drop is a defect in which corrosion is starting. Credit: Frank Vinken

## Conductive polymers are best for capsule walls

In their search for systems that fulfill these requirements optimally in different applications, the two scientists test capsules with different wall materials in various synthetic coatings. The capsules are supplied by researchers working with Katharina Landfester at the Max Planck Institute for Polymer Research in Mainz. Some are spherical in shape, others tubular. Some consist of polymers that dissolve when the pH changes, while others are made of inorganic silicon dioxide that is held together by sulfur "clasps" until they are opened by a drop in potential or an increase in pH. The scientists in Düsseldorf are also working with their colleagues in Mainz to further develop conductive polymers so that they can be used for capsule walls.

While these chain molecules alone can't provide perfect corrosion protection, they have proved their worth as a highly suitable material for the container walls. "Not only do they seal in the components of the plastic coating for good," says Michael Rohwerder, "they become permeable when there is a change in potential." It is precisely this change in electrochemical potential that has shown itself to be the most reliable sign of corrosion.



Raspberry particles is the name the researchers in Düsseldorf use for the capsules that contain the remedy for the plastic coating and bear conductive nanoparticles on their surface (image from a scanning electron microscope, left). The capsules are embedded in non-conductive plastic (blue). Credit: MPI für Eisenforschung

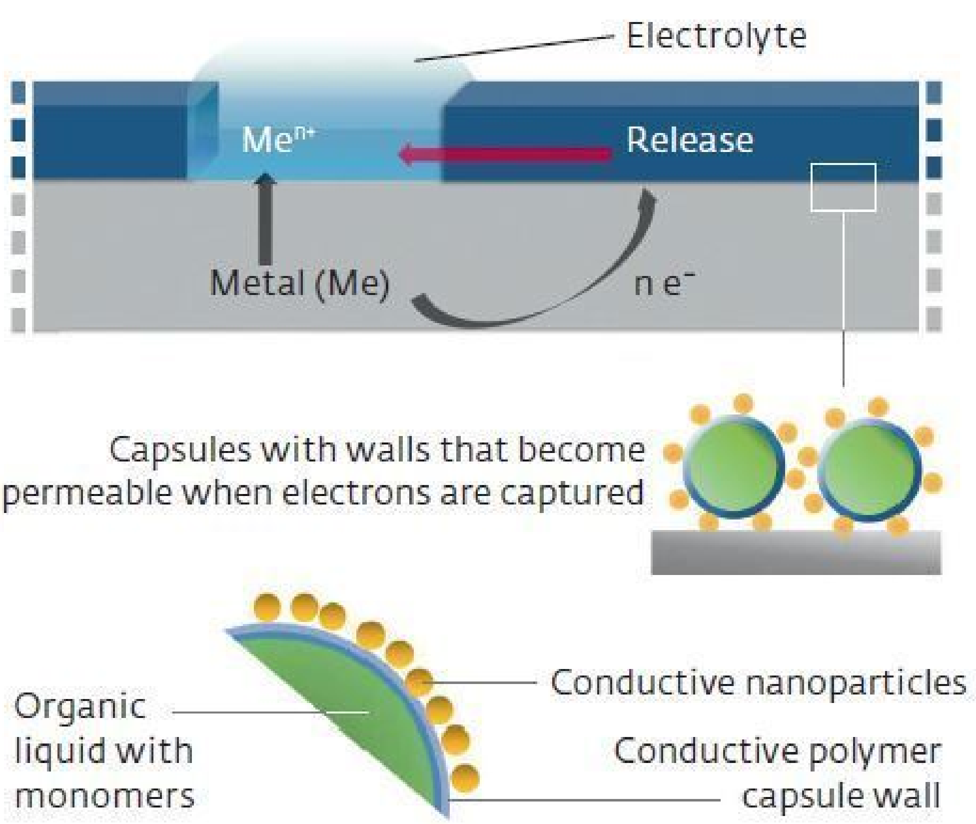
However, the capsules detect this sign only if they are in electrical contact with the buried metal – often zinc. Unfortunately, an insulating layer can easily form between conductive polymers and zinc. "In order to maintain the electrical connection even in these cases, we encase the capsules with conductive nanoparticles," explains Michael Rohwerder. The researchers call the resulting capsules raspberry particles, and a look through the microscope shows this to be entirely justified: the nanoparticles sit on the containers like tiny spheres. Since no insulating barrier forms between them and the zinc underlay, the electrical contact remains in place.

However, self-healing doesn't yet work for containers that release monomers from the plastic coating as required; a catalyst is still needed for this case. This chemical helper will make the healing process possible by mediating the reaction between the monomers. The catalyst must be stored separately from the monomers, while on the other hand, it doesn't remain stable in the organic polymer coating. "That's why we store the catalyst in silicon oxide capsules in the zinc coating," explains Vimalanandan. The catalyst containers open if the pH changes, which is another sign of the onset of corrosion.

Ashokanand Vimalanandan and The Hai Tran monitor whether and to what extent the self-healing with its different factors works by scanning the sample point by point with the Kelvin probe. There are a number of these probes in their laboratory. "It allows us to see whether the hole is closed," says Vimalanandan. But that's not enough for the researchers. They also monitor the progress of the healing process using spectroscopic methods that work with both UV and visible light. "Unfortunately, we still can't look inside the defect," says Tran, "but we are currently testing different methods, like Raman spectroscopy, to try to change that."

Their comprehensive studies show that the ingredients for self-healing can now be stored long-term and dependably released as required. This means that they already meet two of the three requirements, but there's still a hitch with the third: so far, the amount of remedy that flows into the defect is sufficient to close off only scratches of 0.1 millimeters in width. Before they can tackle this issue, the Düsseldorf-based researchers must analyze how the monomers are transported through the coating. "The key question is exactly how the polymer gets into the defect," says Michael Rohwerder.

Despite the unanswered questions, the researcher is optimistic that small damage to metal sheeting will self-heal at some stage. "Chromium(VI) coatings also took decades to develop," says Rohwerder, "so we can't expect to do it in a few short years." And while there are still important gaps in scientific understanding, this only spurs the Düsseldorf scientists on all the more. "After all, we're not in this to solve the everyday problems of industry," explains Martin Stratmann. "We want our research to advance the state of knowledge about corrosion and corrosion protection, and for this reason, we are looking far ahead into the future."



The capsules are embedded in non-conductive plastic (blue). As the diagram shows, the conductive polymer of the container wall absorbs electrons (e-) released into the defect by the corroding metal. The container then becomes permeable and the monomers of the non-conductive plastic flow into the defect, where they polymerize. Credit: MPI für Eisenforschung

## To the point

Corrosion, such as rust, wreaks huge damage. For decades, chromium(VI) compounds were the benchmark in corrosion protection, but they are poisonous and damaging to the environment.

Scientists from the Max-Planck-Institut für Eisenforschung (Iron Research) are now trying to prevent metal corrosion via self-healing polymer coatings that will regenerate when damaged.

These skins for metals contain capsules that store the polymer components permanently and release them without fail when damage occurs, in sufficient amounts to repair cracks of up to one tenth of a millimeter. The scientists are working on self-healing for larger defects. Conductive polymers are particularly well-suited for use as capsule walls.

Provided by Max Planck Society

Citation: Skin with high rust protection factor (2014, June 4) retrieved 26 June 2024 from https://phys.org/news/2014-06-skin-high-rust-factor.html