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New MOF Forms May Lead to New Applications for Warfighter

By Dr. Brian B. Feeney

Aberdeen Proving Ground, MD – In the world of chemical biological defense research, new technologies are typically highly specific and developed in response to a specific threat. Research on metal organic frameworks (MOFs) is the exception because it can meet a wide variety of chemical agent threats. Its applications span protection, decontamination and detection of a wide range of chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) and biological aerosols. They can even be used for gas storage such as oxygen tanks or other forms of supplied air. And now, MOF research is taking another leap in developing this protective material that comes in the form of a bead, a foam, a fiber, or a film, each with its own set of applications for protecting the warfighter.

U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) scientists first started working with MOFs in 2008. Collaborating with research universities such as Northwestern University, Berkeley and North Carolina State plus a variety of small research companies through the Department of Defense Small Business Innovation Research (SBIR) Program and the U.S. Army Manufacturing Technology (ManTech) Program, they have advanced their research into entirely new areas, finding new MOF forms and applications, all to the benefit of warfighters and first responders.

Exactly What is a MOF?

MOFs are nano-constructed materials made of organic struts consisting of oxygen, hydrogen and carbon, and metals, commonly copper, zinc, or zirconium, acting as nodes. Additional functional groups and metals can be added allowing for a vast range of MOFs and resulting in a range of protective properties. They form three-dimensional crystalline structures much like an erector set. The lattice-shaped structures have large void spaces, called pores. The pores are readily filled by whatever liquid or gas flows through it, giving MOFs phenomenal adsorption capacity.

These modular building blocks are organic and inorganic molecular hybrids that take on the advantages of each. The inorganic characteristics give MOFs a very stable compartmentalized structure while the organic component gives them the dynamic quality of interacting with molecules that come into contact with them. Both the organic and inorganic components can be interchanged to create an incredible variety of structures and properties designed to absorb or catalyze chemical warfare agents, toxic industrial chemicals and other gases as desired. Thus, MOFs are truly nano-constructed designer materials.

"Metal-organic interactions have been known for decades; however, only in the late 1990s and early 2000s did research on MOFs accelerate because of the energy industry's interest in their potential for capturing and storing hydrogen gas," said DEVCOM CBC chief scientist Greg Peterson. His initial interest in MOFs was in creating a MOF that would vastly improve upon the carbon filters that Soldiers and first responders have relied on since World War I. As his research has progressed over the last 16 years, he and his research team have developed ever more capable MOFs that can perform a wide variety of functions.

Starting in 2016, the Center started funding small research startup companies through the SBIR program to take these improved MOFs from the milligram-production phase created in academic research laboratories up to quantities suitable for commercial production.

New Applications, and the Bead Goes On

In 2020, the team started performing research into how their MOF crystals could be placed inside beads not only to trap chemical agents, but to detoxify them once trapped. They received funding from the Defense Threat Reduction Agency and transitioned the technology to the U.S. Army Soldier Center in Natick, Massachusetts which is responsible for researching how to make warfighters' uniforms more protective. Together they worked on placing multiple MOF crystals in a single bead, each crystal designed to detoxify a different agent.

The trick they mastered was to place inside the same bead a MOF crystal for neutralizing base agents and another MOF crystal for neutralizing acidic agents in a way that prevents them from interfering with each other as would normally be the case. They also succeeded in making the beads squishy so that they do not fracture under pressure. They now have MOFs in a form that can ultimately enhance the carbon routinely used in respirators.

Peterson and his team decided that they also wanted to find a way to stick their beads directly on to fibers. They went to a commercial fabric store to find a nylon that would work. They ironed on decals containing the MOF crystals and discovered that this simple method actually worked well for adhering their crystals to a combat uniform. They then introduced the technique to small startup companies participating in the SBIR Program for them to scale up for commercial production.

Foam: Getting the Filter Off the Face

At the same time they were pursuing beads, Peterson and his research team knew that they wanted to get chemical agent filters off the face of warfighters while providing the same protection. Wearing a filter over the nose and mouth is uncomfortable and degrades combat effectiveness.

They began working with the U.S. Army Research Laboratory and North Carolina State University to find ways to make MOF-containing filters squishy so that a rifleman can press his chin against the stock of the rifle to take aim while wearing a mask. Foam also allows for moving the filter to a less obtrusive location such as integrating it into the foam already being used for shock and ballistic protection on the top of head. The air inside the helmet gets filtered on the head and circulated down to the nose and mouth. In addition, MOF foam can be 3D printed.

This research has been promising and the team is ready for a seat at the design table for the next generation helmets and uniforms so that their MOF-based nanotechnology solutions can be put to full use.

Breathable Fibers Instead of Butyl Rubber

Fibers impregnated with MOFs can be used in a scarf for escape purposes, used in decon wipes, and used in curtains to provide collective protection in rooms. MOF-impregnated fibers can even be used in submarines to capture carbon dioxide that accumulates inside submarines on long dives.

MOF fiber spinning has advanced, too. For many years, Peterson and his team were using a method called electrospinning. It uses an electrical charge to turn a liquid polymer solution into many nanofibers that provide an ideal surface to deposit MOFs. They also can be blow-spun using compressed air or melt-spun using heat to melt the polymer. Currently, they are optimizing a technique based on blow-spinning in which they use compressed air instead of a high voltage to turn a liquid polymer solution into nanofibers. They are also working with North Carolina State University's Nonwovens Institute to build a melt spinner that will melt the polymer and then spin into fibers without the use of strong solvents.

Films

MOF films are similar to a fiber swatch but rubbery. They are created by dropping a solution of MOF and polymer on a flat surface and flattening the drops out with a blade, much like how a baker covers a cake with frosting. After being flattened, it dries out and can be pulled up for use as a protective material. Uses include anything currently constructed of butyl rubber such as masks, gloves and boots. A valuable feature of MOF film is that, unlike butyl rubber, it is moisture wicking. That relieves the wearer of much of the discomfort that comes with most protective personal protective equipment. Peterson and his team used the SBIR program to have it further developed by small technology companies.

Still More Applications and a Bright Future

Still other applications include using MOFs for water harvesting. MOFs pull moisture out of the atmosphere which means that they can be used to create potable water in the desert. MOF-infused material can also be used for agent detection by designing them to change color or fluoresce in the presence of agent. MOFs may even one day be designed to provide drug delivery by having them absorb a medicine then injecting them into the bloodstream for timed release.

This long-term Defense Threat Reduction Agency (DTRA) funded effort has allowed DEVCOM CBC researchers to meet an ever- widening array of warfighter and first responder needs and has created many opportunities to work with non-traditional defense contractors. Two of these companies have had their MOF-based technologies showcased at the annual DTRA in-the-field user assessment of chemical, biological, radiological and nuclear (CBRN) technology known as Chemical and Biological Operational Analysis (CBOA).

Mainstream Technologies, a Florida-based technology developer, will have a tabletop display of its product, MOFSorbents, at the next CBOa. It enhances chemical agent protection for garments, filters and masks. Tetramer Technologies, a Clemson, South Carolina technology developer, featured its MOF-based Next Generation Tactile CBRN Gloves in a tabletop display.

Reflecting on a Long Research Journey

Peterson has devoted more than a decade of his professional life to MOF research. Looking back on it, he expressed satisfaction. “It has been very rewarding for me to get MOFs to where they are right now, but there is still work to do,” he said. “We have taken these powders that were originally made in milligrams amounts to the ton production scale and put them into various prototypes in filtration, decontamination, and protective suits. We are putting MOFs into new functional forms that could revolutionize how we do chemical biological protection. There are non-military opportunities, too. MOFs are extremely well-suited for water harvesting, water purification and reuse, gas storage, and more.”

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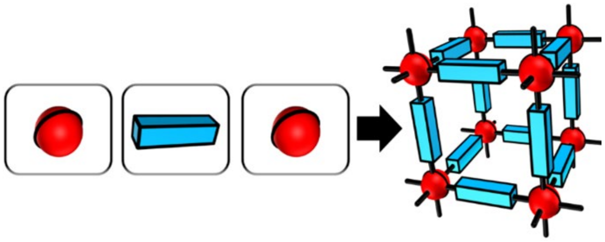
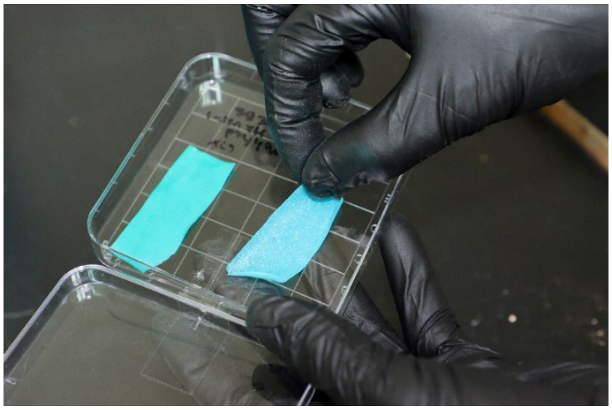
For more information about the DEVCOM Chemical Biological Center, visit https://cbc.DEVCOM.army.mil

DEVCOM CBC chief scientist Greg Peterson, who leads the MOF research team, holds two containers of MOFs in their bead form. (U.S. Army photo by Ellie White.)



MOFs are metal oxide clusters connected by organic linkers, resulting in formation of 3-dimensional, highly porous, crystalline structures.

In the form of a squishy foam, MOFs can be used in gas masks that interfere less with a Soldier's ability to aim a rifle. (U.S. Army photo by Ellie White.)



In the form of film, MOFs can be used for everything from masks, gloves and boots. (U.S. Army photo by Ellie White.)

The U.S. Army Combat Capabilities Development Command, known as DEVCOM, is Army Futures Command's leader and integrator within a global ecosystem of scientific exploration and technological innovation. DEVCOM expertise spans eight major competency areas to provide integrated research, development, analysis and engineering support to the Army and DOD. From rockets to robots, drones to dozers, and aviation to artillery, DEVCOM innovation is at the core of the combat capabilities American Warfighters need to win on the battlefield of the future. For more information, visit devcom.army.mil.

The DEVCOM Chemical Biological Center is the primary DOD technical organization for non-medical chemical and biological defense. The DEVCOM Chemical Biological Center fosters research, development, testing and application of technologies for protecting our military from chemical and biological warfare agents. The Center possesses an unrivaled chemical biological defense research and development infrastructure staffed by a highly-trained, multidisciplinary team of scientists, engineers, technicians and specialists located at four different sites in the United States: Edgewood Area of Aberdeen Proving Ground, Maryland; Pine Bluff Arsenal, Arkansas; Rock Island Arsenal, Illinois; and Dugway Proving Ground, Utah.