Surface properties command attention

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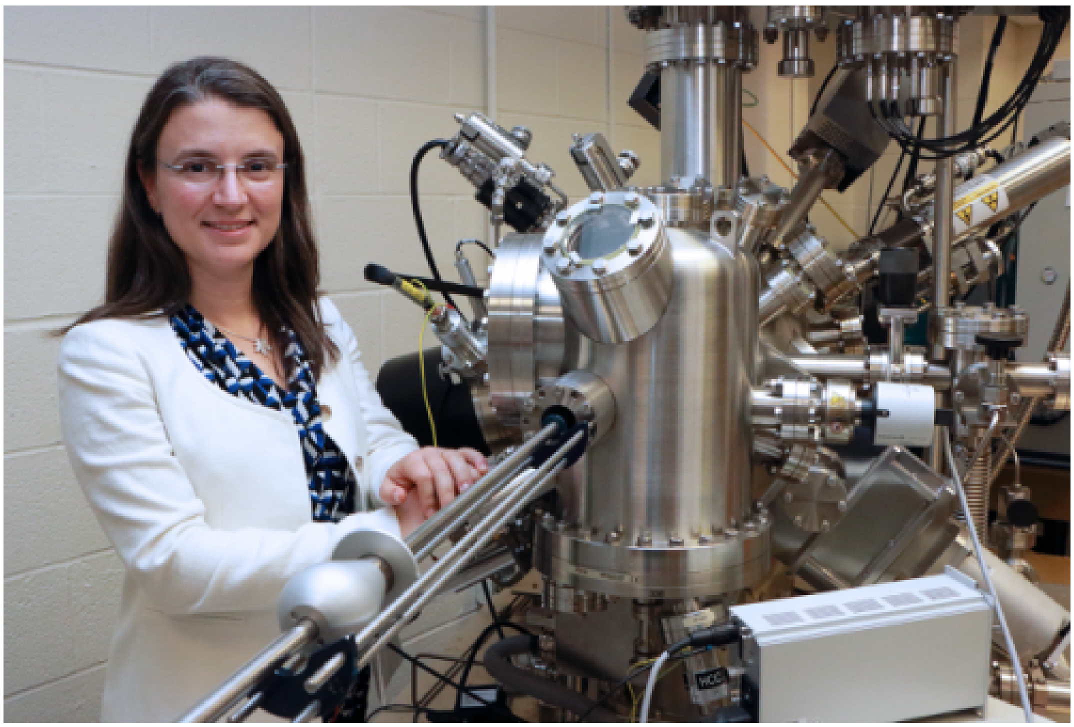


Bilge Yildiz with a scanning tunneling microscope customized to study oxide material surfaces at high temperatures under mechanical stress in the presence of oxygen, water vapor, or other reactive gases. Credit: Denis Paiste/Materials Processing Center

Whether working on preventing corrosion for undersea oil fields and nuclear power plants, or for producing electricity from fuel cells or oxygen from electrolyzers for travel to Mars, associate professor of nuclear science and engineering Bilge Yildiz is motivated by a desire to understand the underlying physical phenomena that govern surface reactions.

"The work we do in our lab focuses first on the mechanisms of whatever phenomenon in which we are interested and curious about. Based on that understanding, we then guide design of new materials," Yildiz says.

Yildiz will be a guest speaker at the Materials Day Symposium, New Frontiers in Metals Processing, on Oct. 21, and will outline her work uncovering the inner workings of metal corrosion by combining surface sensitive experiments and multi-scale modeling.

Stretching oxides to improve performance

One area that her group explores is the use of small elastic strains to improve the electrochemical and transport properties of metal oxide thin films for better fuel cells, electrolyzers and other uses. "I think we have come quite a long way in the last few years in explaining how strains can impact the diffusion and reaction kinetics. Both our new knowledge of what elastic strain can do to transport and reactions, and what we are now uncovering about the role of dislocations together, are important in strain engineering of such materials for electrochemical systems," Yildiz says.

"By combining experiment and theory, we were able to uncover the mechanisms for how this can happen," she says. Her lab has shown that by making nanoscale elastically strained thin oxide films, one can significantly alter the formation energy, or thermodynamic equilibrium, of oxygen vacancies that are critical for the performance of these materials. They also demonstrated that strained oxide films can alter the electrochemical performance of the electrode by reducing the energy barriers in the transport of vacancies and transfer of charge at the surface.

Taking the next step toward developing devices based on this research will require re-engineering of the microstructure of fuel cells and electrolyzers to incorporate strained thin films. However, it is doable, Yildiz says.

Among members of Yildiz's Laboratory for Electrochemical Interfaces, graduate students Lixin Sun and Qiyang Lu are working on effects of elastic and plastic strain on transport and reactivity properties of oxides, while postdoc associate Mostafa Youssef and graduate students Aravind Krishnamoorthy and F. William Herbert are studying corrosion and hydrogen absorption through surface films.

Ionic freeway or traffic jam?

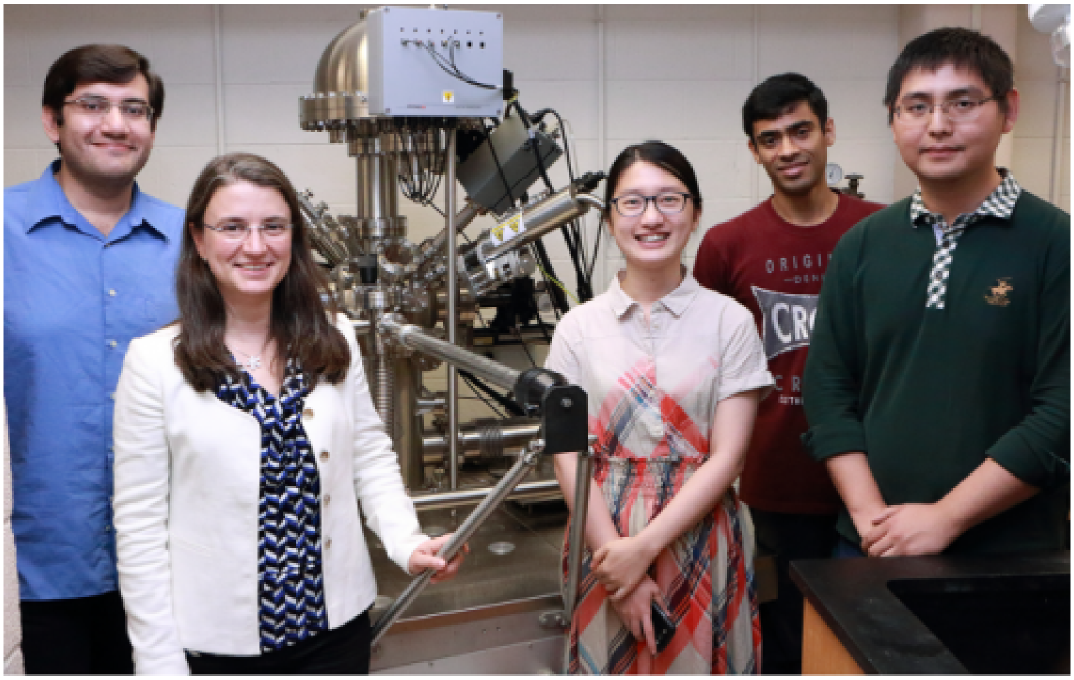
Sun's research investigates whether or not oxide electrolytes for fuel cells have dislocations (that is, plastic strain) that serve as fast oxygen diffusion paths. She likens the process to a freeway for speedy cars—if the dislocations allow for fast diffusion—or a traffic jam along the dislocations—if dislocations do not permit fast diffusion of oxide ions.

For better performance, the oxide ion diffusion should be fast. Dislocations, which are defects in the microstructure of a material, are fast pathways for atom transport when they are present in metals. But Sun's research in the Yildiz group investigates whether this is true for all oxides. "When you come to the oxides that we use in fuel cells, electrolyzers, membranes, that have intrinsically fast ion conduction, this concept of 'freeway dislocations' needs reconsideration, because such oxides have charged defects and the electrostatic interactions among those charged defects may lead to the trapping of oxygen. Such strong electrostatic interactions do not occur in metals. The fast-path assumption adopted directly from metals to oxides may not work for the design of oxide microstructures," Yildiz explains.

Lu, Sun's colleague, focuses on oxygen exchange on the surface of cathode material and the effect of elastic strain on the kinetics of surface reactions.

"The motivation is to lower the operating temperature of solid oxide fuel cells; however, both the ion diffusion and surface reactions are thermally activated. But you need a certain temperature to maintain high efficiency. So what we can do is to use lattice strain to enhance materials properties, for example, accelerate the cathode reactions or oxygen diffusion in the electrolyte to maintain the same conversion efficiency at the lower temperature. That's the final goal that we are fighting for," Sun says.

While Sun and Lu work to enhance oxygen reduction reactivity on thin film surfaces for electrolytes and cathodes of fuel cells, Krishnamoorthy and Youssef are working to reduce corrosion rates by reducing the reactivity on thin sulfide and oxide films that form on surfaces of pipes for pumping undersea oil or cooling nuclear fuel in reactors. "While they (Qiyang and Lixin) are trying to make surfaces more reactive, we are trying to make them more inert, more stable, so that the underlying metal is more protected," Krishnamoorthy says.



Members of the Laboratory for Electrochemical Interfaces at MIT include (from left) postdoctoral associate Mostafa Youssef, Yildiz, and graduate students Lixin Sun, Aravind Krishnamoorthy and Qiyang Lu. Credit: Denis Paiste/Materials Processing Center

Hydrogen at play on surfaces

Zirconium oxide forms as a thin native film during corrosion of zirconium alloys in nuclear reactors and serves as a barrier to corrosion and to hydrogen intake into the metal. Youssef and Yildiz reported last fall that defects in tetragonal zirconium oxide, such as missing oxygen or zirconium atoms in the crystal structure, could be filled by hydrogen atoms leading to degradation of the material. The simulation found that "zirconium vacancies can act as trapping sites for hydrogen and the resulting complexes can be detrimental precursors for mechanical failure of the oxide." They currently are evaluating the impact of differing zirconium alloys on preventing hydrogen uptake through the zirconium oxide layer, which is a cause of premature fracture.

A more recent study by Yildiz, Youssef, and Wen Ma, with lead author Uuganbayar Otgonbaatar, modeled the effect of niobium in the corrosion resistance of zirconium oxide. While niobium-zirconium alloys are considered for and used in advanced nuclear materials, the sole effect of niobium on corrosion was still not understood. Their work uncovered that, if the corrosion rate is limited by oxygen transport, as could be in the early phases of corrosion, niobium improves corrosion resistance by suppressing the oxygen transport through the zirconium oxide layer.

Battling against surface aging

Another type of oxide materials, perovskite oxides, used in fuel cell cathodes and other devices behave differently (in a bad way) at their surface than in their bulk, Yildiz's research has demonstrated—especially under harsh conditions, such as high temperatures, and in the presence of reactive gases, such as oxygen, water vapor and carbon dioxide.

"Many of the perovskite oxides that we have studied have an inferior surface because of compositional and phase changes compared to the bulk material," Yildiz says. Not only do they have different crystal structures on the surface caused by aging, but they also have different electronic structures, often becoming more insulating, compared to the bulk. "The surface is where we have charge transfer reactions to oxygen, and if you have to deal with these unwanted phases, then your surface reactions are all slowed down because of the formation of these insulating phases."

"We have also uncovered what are the driving forces to this, so that now we are in the process of making materials, or surfaces, that do not undergo degradation as much as the traditional materials that we have seen, or even in some cases no degradation at all," Yildiz adds. That work is continuing and hasn't been published yet, but, "We have laboratory results that show we might be going in the right direction."

New lab techniques

Much of Yildiz's research has been enabled by scanning tunneling microscopy and other techniques that allow her to exam oxide materials at high temperatures under mechanical stress in the presence of oxygen, water vapor, or other reactive gases. While early scanning tunneling microscopes functioned in ambient conditions or ultra-high vacuum, those conditions were not suitable for her investigations, so Yildiz worked with a company to customize one of their instruments for the environments she needed to study. "We were able to uncover these responses of the material surfaces to those difficult environments that were not seen before. So that's an experimental enabler that we have developed in our group," she says.

Breakthroughs in electrolyzers or fuel cells could enable secondary products at nuclear power plants in addition to their direct electricity production, for example, by using the heat from reactors to electrolyze water, or water and carbon dioxide together. "If you electrolyze only water vapor, you get hydrogen; if you electrolyze water vapor and CO2 together, you get synthetic gas that can then be made into liquid fuels," Yildiz explains. "The CO (carbon monoxide), H2, output is what we need for making liquid fuels, and this approach can expand the use of nuclear energy beyond electricity."

Oxygen for astronauts

In a collaboration with MIT's Department of Aeronautics and

Astronautics, Haystack Observatory, and industry, Yildiz is working on an oxygen-production unit for NASA's Mars 2020 mission. The MOXIE instrument will use a reverse fuel cell to produce oxygen from electricity. Haystack assistant director for research management Michael Hecht is principal investigator for the project. Yildiz's lab will focus on carbon dioxide (CO2) electrolysis to make oxygen for the Mars mission. "I don't want the astronauts to run out of oxygen when they are there," she says. "We'll be looking at how the surfaces of oxide electrocatalysts respond to a CO2 environment (that is abundant in Mars) and what are the reaction mechanisms, so that we can design materials that are more durable as well as more active compared to what we have existing from fuel cells."

Yildiz worked with researchers at Idaho National Lab and Ceramatec Inc. on studies of degradation in solid oxide electrolysis cells (SOECs) designed for generating hydrogen from high-temperature electrolysis.

Oxide mechanics probed from electrons

Yildiz has several mentors at MIT, including Professors Sidney Yip (nuclear science) and Harry Tuller (materials science). Yildiz works with Tuller's Department of Energy-funded COFFEI (Chemomechanics of Far-From-Equilibrium Interfaces) research project, which couples chemical and mechanical behavior of electroceramic oxides. These materials have potential uses in fuel cells, electrolyzers, ion transport or separation membranes, and memory logic devices called memristors. "Our investigations in part probed how mechanical stresses impact the reactivity of these materials with their environment and transport of oxygen ions through them," Yildiz says. "We would like to accelerate all these reactions and transport processes in order to make these devices higher performance, but also make sure the material lasts long. It turns out the mechanical failure of these oxides is impacted by their defect chemistry, a problem that we worked on computationally."

Tuller and Yildiz were among an international group of collaborators who won the Somiya Award in 2012 for their work on designing ionic and mixed conducting ceramics for fuel cell applications. A collaborative paper with lead author Dario Marrocchelli, then a postdoc associate in Yildiz's lab, showed computationally that chemical expansion of cerium oxide, used in fuel cells, is because of an increase in charge localization around positively charged cerium ions.

"When you change the chemistry, you also change the mechanics of the material," Yildiz explains. "We performed computational work to understand the mechanism by which this happens, and that is, as you remove an oxygen from the lattice, you leave behind electrons, and those electrons go and localize on the metal ions and increase their size. This effective size increase tries to expand the lattice and, if you have a gradient of this expansion, then you can lead to a fracture of the material." Based on the theoretical finding, experimental researchers in Tuller's group are testing materials that could be more resilient against this degrading problem, she says.

Taking on challenges

Yildiz, who grew up in the coastal town of Izmir in Turkey, studied nuclear energy engineering as an undergraduate at Hacettepe University in Ankara. But Turkey does not have a nuclear reactor, so Yildiz came to MIT to study for her PhD. Her doctoral thesis focused on artificial intelligence algorithms for predicting failures in nuclear reactors. "This was a combination of math and computer science, which was also interesting, but I feel that I am more of a physical science person," she says.

She chose a postdoc post at MIT, and then a research scientist position at Argonne National Laboratory, where she could work on physical chemistry and electrochemistry on surfaces. "It's quite different than what I have formal education on during my PhD work," she says. "I don't think I knew or even thought it was challenging at the time. I was interested in that topic, so I wanted to work on it. But now when I look back on it, I realize it was challenging." She tells her students now what her PhD advisor told her: The PhD means you are qualified to do new things.

Yildiz and her husband, Audun Botterud, have a two-year-old son, Ege. Botterud is an energy systems engineer with Argonne National Lab, and a visiting scientist with MIT Energy Initiative. He has a PhD in industrial engineering and electrical engineering and models how to integrate new clean energy technologies into the power grid.

Yildiz is developing a new course for next spring on surface science. She also teaches 22.11 (Applied Nuclear Physics), a core graduate student class that covers nuclear structure, reactions, and radioactivity, and co-teaches 22.070 (Materials for Nuclear Applications), which draws on her work on degradation of materials in harsh environments.

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