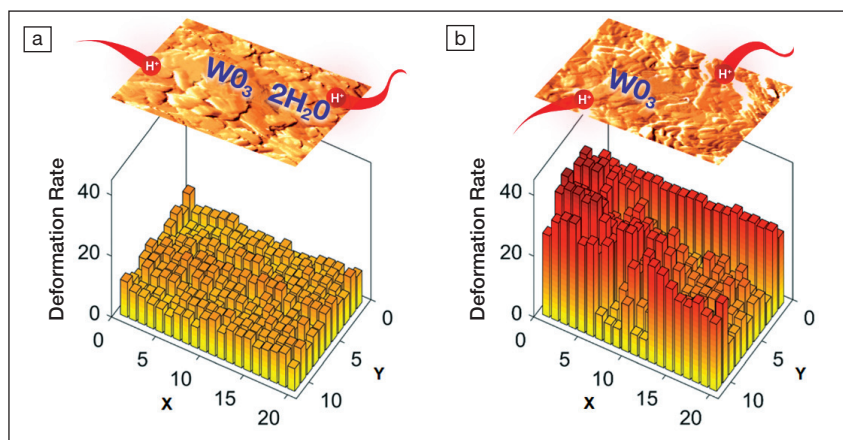


response to hydrated, two-dimensional tungsten oxide ($\text{WO}_3 \cdot 2\text{H}_2\text{O}$) electrodes that contain water. They reported their findings in a recent issue of *ACS Nano* (doi: 10.1021/acsnano.8b02273).

“The exciting aspect about the correlation between the electrochemical current and electrode deformation measured via AFM is that it allows us to probe electro-chemo-mechanics at the nanoscale,” Augustyn says. “This was particularly helpful in elucidating the unexpected role of water incorporated into the structure of the hydrated form of tungsten oxide.”

“We found that the water layers in hydrated tungsten oxide do two things,” says Ruocun Wang, a doctoral student in Augustyn’s laboratory and lead author of the article. “First, they minimize deformation and reduce expansion and contraction of the material as ions move in and out. Second, the water layers make the deformation more reversible, meaning that the material returns to its original dimensions more easily,” he says.

The researchers used a platinum-coated AFM cantilever to measure deformations in tungsten oxide electrodes while they applied an electrochemical cycling experiment with a sulfuric acid electrolyte. The shapes of charge–discharge cyclic voltammetry curves corresponded with the mechanical deformation rate of the respective electrodes. Of note, electrochemical results contrasted the pseudocapacitive-like behavior of hydrated WO_3 (fast, reversible surface reactions) against



Scanning probe microscopy captures the flexibility of tungsten oxide electrodes during electrochemical cycling and highlights the relative ease with which ions enter and exit the hydrated electrode form (a) compared to the anhydrous electrode (b). Credit: Veronica Augustyn et al.

the battery-like intercalation process in its anhydrous counterpart (slow, diffusion-limited process).

Anhydrous tungsten oxide experienced significant strain in order to intercalate the protons into its structure, and the asymmetrical profile of its charge–discharge cycling behavior mirrored its AFM-detected mechanical deformation rate. Structural analysis of the hydrated material showed that water molecules in the interlayer spacing separated the layers of corner-sharing $\text{WO}_5(\text{OH}_2)$ octahedra and confined the deformation to two dimensions. This, in turn, endowed the hydrated form with greater flexibility and allowed ions to easily move in and out of the electrodes during cycling.

Albert Davydov of the National Institute of Standards and Technology, who was not involved in this study, says, “*In situ* correlation of reversible redox activity with the mechanical deformation, together with high spatial and temporal resolution of the AFM dilatometry, has unambiguously inferred the proton exchange mechanism in hydrated versus anhydrous tungsten trioxide. I can envision how this methodology can be extended to gain an insight into the reaction mechanisms in other industrially relevant electrochemical processes, such as catalysis or corrosion.”

Other members of the research team are affiliated with Oak Ridge National Laboratory and Texas A&M University.

Boris Dyatkin

Bio Focus

3D printed scaffolds developed from isomalt sweetener

Three-dimensional (3D) printing is one of the fastest-growing industrial technologies, but it still lacks versatility. Commercial 3D printers typically use brittle plastics that have limited biocompatibility and cannot print hollow or unsupported structures. Now, a group of researchers from the University of Illinois at Urbana-Champaign has developed a way to 3D-print open structures using an artificial sweetener called isomalt. This

paves the way to more biocompatible 3D printed structures that can be used to grow artificial organs and veins.

In order to be used as a scaffold for growing organs and blood vessels, the printed objects need to be easily dissolved after cells have grown on them, while still being strong enough to hold a 3D structure. It is also important that the material, when solid, forms a glass rather than a crystal, so that it can cool into its desired shape without clogging the printer. The class of materials that fits this bill is the sugar alcohols, similar in chemical structure and used as

sweeteners, which can form carbohydrate glasses when they solidify.

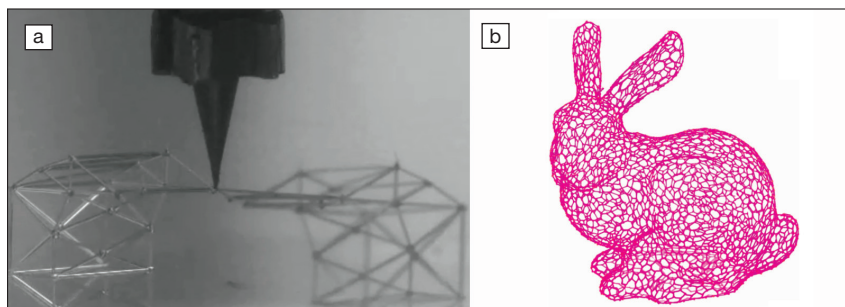
While several sugar alcohols were tested, the best candidate was isomalt, a sweetener used in sugar-free candy, because it is stable at room temperature and resists crystallization as compared to other sugar alcohols. “We especially focused on using isomalt as it is readily processed and has excellent biocompatibility,” says Rohit Bhargava, who led the research team. “However, its use also needs a careful analysis and validation of the printing process,” he says. As the research group reported in a recent issue of



Additive Manufacturing (doi:10.1016/j.adma.2018.04.026), the two principal challenges that had to be overcome were the dehydration of the isomalt and its stability during the extruding process.

Isomalt forms crystals in the presence of water, but remains glassy when dehydrated. Dehydration was achieved by stirring the isomalt in a vacuum to eliminate any dissolved water. Debugging the extrusion process was more challenging. The material needs to quickly solidify as it cools, while maintaining its desired printed shape.

Most 3D printers operate by depositing horizontal layers on top of one another, making structures thick enough to support their own weight. In contrast, the objects the researchers printed were hollow and made entirely of thin rods. Furthermore, the research team faced challenges and structural issues that do not arise during traditional 3D printing, which include thermal contraction as the material cools, the sagging of the rods under gravity, the momentum imparted in the fluid by the moving nozzle, and the inherent viscosity



(a) The extruding nozzle in action, printing the scaffolds for a bridge. (b) A hollow 3D printed bunny with pink dye added. Credit: Images adapted from *Additive Manufacturing*.

of the rods. Through numerical models the researchers determined that the printed beams are stable if they are thinner than the extrusion nozzle. They then proved their concept by printing structures out of rods that would be impossible with traditional 3D printing methods, including truss bridges and hollow bunnies.

The ultimate goal is to be able to use these 3D printed structures as scaffolds for cell culture to grow organs and blood vessels for transplantation. “The first step was

to establish the scaffold printing process, which we report in this study,” Bhargava says. “The next step is to deposit and grow cells in a supported manner on these scaffolds. The third major step is to remove scaffold materials such that biological activity is minimally affected and the fabricated tissue structure is structurally stable.” If all goes well with the development of this technology, we can look forward to both lifesaving and delicious printed structures.

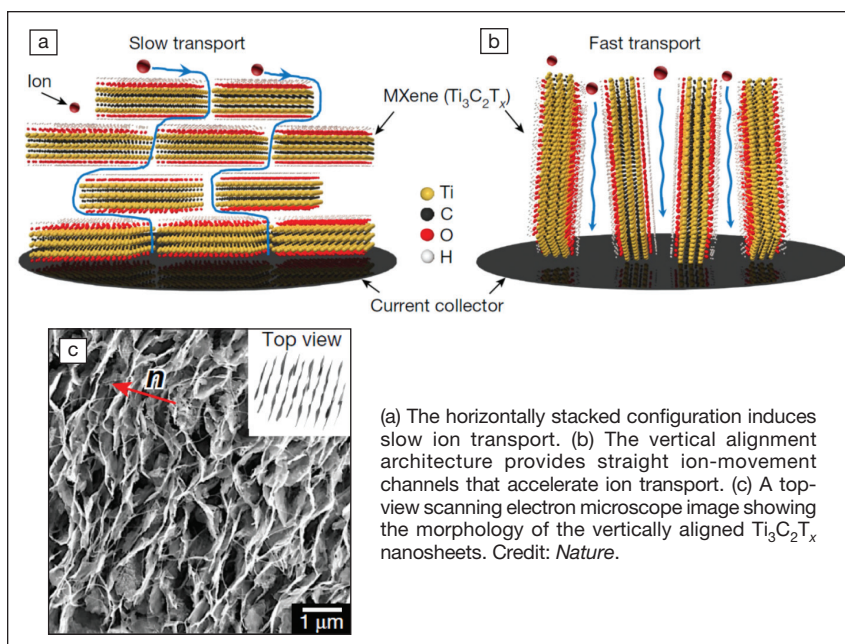
Alex Klotz

Nano Focus

Vertically aligned MXene nanosheets speed up supercapacitor

The practical potential of MXenes (two-dimensional, a few atoms thick layers of transition-metal carbides, nitrides, and carbonitrides) as supercapacitor electrodes has become more promising with the successful vertical alignment of MXene nanosheets on substrates. These electrodes exhibit ultrafast charging capabilities. This leap in energy storage, published recently in *Nature* (doi:10.1038/s41586-018-0109-z), was achieved by the collaboration between Shu Yang’s group at the University of Pennsylvania and Yury Gogotsi’s group at Drexel University.

The conventional configuration is composed of horizontally stacked MXene sheets that is undesirable for fast-rate charging as ion diffusion through the sheets is severely impeded by the compact-film configuration. The sluggish ion movement leads to deterioration



(a) The horizontally stacked configuration induces slow ion transport. (b) The vertical alignment architecture provides straight ion-movement channels that accelerate ion transport. (c) A top-view scanning electron microscope image showing the morphology of the vertically aligned $\text{Ti}_3\text{C}_2\text{T}_x$ nanosheets. Credit: *Nature*.

of energy-storage capacity at elevated charging rates. This problem is exacerbated when the film thickness approaches or exceeds $10\ \mu\text{m}$, far less than the industrial thickness standard of $100\ \mu\text{m}$

for active materials used in supercapacitors. To resolve this issue, developing electrodes with straight ion-movement channels extending from the electrode surface to the substrate is critical.