



Understanding the mechanism of perovskite degradation is key to designing more stable perovskite solar cells. In a recent *Nature Communications* (doi:10.1038/ncomms15218) study, researchers reported insights on why methylammonium lead iodide perovskites undergo degradation when exposed to oxygen and light.

The team from Imperial College London and the University of Bath previously found that in the presence of light, oxygen molecules scavenge photogenerated electrons to form highly

reactive superoxide species, which can quickly degrade $\text{CH}_3\text{NH}_3\text{PbI}_3$.

For the study, they combined experimental and computational methods for a microscopic assessment of the mechanism. They exposed a 500-nm-thick $\text{CH}_3\text{NH}_3\text{PbI}_3$ film to dry air for 20 minutes while recording its weight. The film saturated with oxygen within 10 minutes. Time-of-flight mass spectrometry showed the gas was uniformly distributed in the film.

Films made of 100 nm crystals had much more superoxide yield than

those with larger 250 nm crystals, so they degraded within two days as opposed to nine for the latter. Further, *ab initio* simulations showed that vacant iodine sites acted as traps for oxygen molecules and electrons, facilitating superoxide formation.

When the researchers coated the perovskite film with iodide salts, the films remained stable for more than three weeks of oxygen and light exposure, because the salts filled iodide defects in the film, which suppressed the superoxides.

An ink developed for perovskite thin films reported recently in *Nature Energy* (doi:10.1038/nenergy.2017.38) should allow the manufacture of perovskite films on large areas at high volumes, important for producing solar photovoltaic modules commercially.

Most researchers make perovskite films using spin coating, which involves depositing a precursor solution on a fast-spinning substrate, evaporating the solvent, and then heating the film. This is hard to accomplish quickly on a large

scale. Antisolvents are typically added during spin coating to rapidly saturate the perovskite crystals out of the solution, which gives uniform films. But the window for this processing step is only a few seconds, making it difficult for large-scale manufacturing.

Kai Zhu and Maikel van Hest, at the National Renewable Energy Laboratory, formulated an ink of $\text{CH}_3\text{NH}_3\text{I}$ and PbI_2 in a *N,N*-dimethylformamide solvent and added an excess of methylammonium chloride.

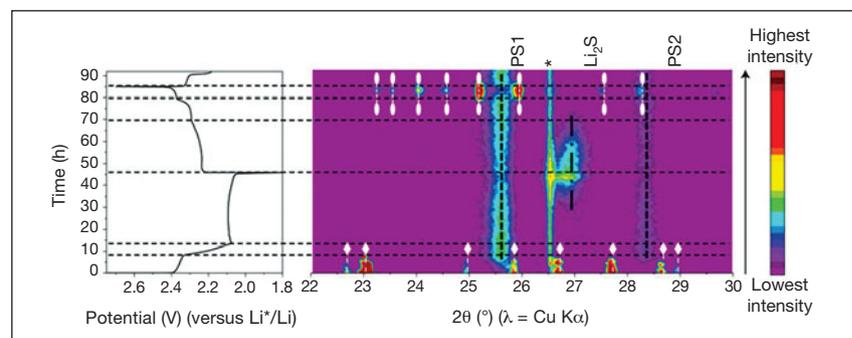
The ink can be deposited on a substrate using blade coating, an easily scalable processing method used to make large-area films on rigid or flexible surfaces in which a blade spreads liquid on a moving substrate. Instead of seconds, the precursor ink film can be processed for up to eight minutes. Further, it only needs a minute of heat treatment. All of this would be attractive for manufacturing. The researchers used the process to make 1.2 cm^2 cells that had an efficiency of 17.33%.

Energy Focus

Operando XRD captures soluble polysulfide intermediates in lithium-sulfur batteries

A research team led by Claire Villevieille of the Paul Scherrer Institute used *operando* x-ray diffraction (XRD) to observe soluble polysulfide intermediates in a lithium-sulfur battery. This study, which expands the battery-characterization capabilities of *operando* XRD, was published recently in *Nature Energy* (doi:10.1038/nenergy.2017.69).

Lithium-sulfur batteries are a potential replacement for the ubiquitous lithium-ion batteries that are found in cell phones, computers, and electric cars. That is, if the formation of parasitic polysulfide intermediates can be characterized and controlled in these batteries. “To date, we haven’t found a proper solution to the problem in lithium-sulfur batteries:



X-ray diffraction (XRD) contour plot of the XRD patterns (right), with the corresponding galvanostatic curve (left) recorded during the first cycle of the lithium-sulfur battery. The intensity chart is given at the very right. The asterisk refers to a peak arising from a cell part. $\alpha\text{-S}_8$ and $\beta\text{-S}_8$, the two polymorphs of sulfur formed at the cathode, are represented by white vertical lines with diamond and oval symbols, respectively. The positions of the peaks labeled PS1 and PS2, attributed to the polysulfide-silicon dioxide interactions, are indicated by vertical black dashed lines. Li_2S refers to the solid end-of-lithiation product lithium sulfide, and is symbolized by a dashed-dotted black vertical line. Overall, the horizontal dotted black lines are used as guides for following the changes in the peaks intensity as a function of the potential/time. Credit: *Nature Energy*.

when the sulfur, which is a solid, starts to be cycled in the battery, it turns into a liquid, forming various polysulfides,”

Villevieille says. The continuous loss of sulfur material during this process results in decreased capacitation over time, and

a reduction in lithium-sulfur battery performance. To combat this, researchers have engineered many ways to trap the polysulfide intermediates, developing trapping layers or separators to keep the intermediates on the sulfur cathode. Understanding how these intermediates form and how they interact with the materials used to contain them could lead to the development of better trapping layers.

“Characterizing the polysulfides, which is required to figure out ways to mitigate their formation or trap them, has been a challenge,” says Michael Toney, of the Stanford Synchrotron Light Source. Toney also uses XRD and imaging techniques to characterize electrochemical materials, but was not connected with this work. Scientists have used x-ray and UV-visible absorption spectroscopy to try to capture the formation and migration of these intermediates, but such methods

lack precise characterization of their location and quantity in the cell. XRD has been used to study the structure of the solid components of the battery in great detail, but it would not have been possible to see the polysulfides, which lack long-range order when they are dissolved in the electrolyte.

Because of this, Villevieille’s group anticipated only observing the solid electrodes in the XRD experiment and seeing how changing the separator layer between them would alter their structure. They started using silica fibers as a simple separator material. They were surprised to see two unknown peaks appearing in their XRD diffractograms when they expected to see none.

“If the liquid [polysulfides] are visible,” Villevieille says, “[this means that] it’s deposited as a layer somewhere.” Further characterization of the separator

using electron microscopy revealed that the polysulfides had adsorbed onto the silica fibers of the separator. Suspecting an interaction between the silica and the polysulfides, Villevieille’s group used a polymer separator. The peaks disappeared when the polymer separator was used but reappeared when fumed silica was added to the electrolyte solution. “When there is silicon dioxide, we see the signature,” Villevieille says.

Villevieille does not think that this effect is limited to silicon dioxide alone and is currently testing other oxides to scavenge the polysulfide intermediates. Her next step is to demonstrate how this technique can be used to optimize the battery cycling stability. These future measurements and others like it are “going to be valuable for informing the community on how to move forward,” Toney says.

Lauren Borja

Bio Focus

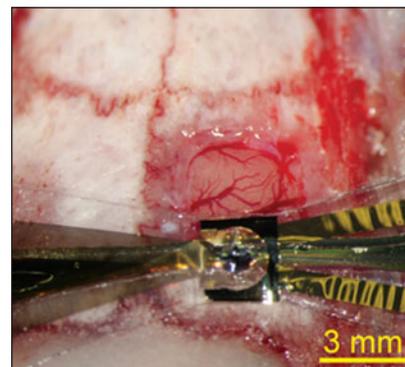
Microfluidic device delivers drugs directly to brain

Various neurological disorders, from Parkinson’s disease to major depression, are treated using drugs that are delivered systematically, ultimately affecting tissues throughout the body indiscriminately. To avoid the inevitable side effects of these drugs, researchers are developing implantable devices that deliver drugs locally to the brain and nervous system. In a step forward, an international team of researchers has developed an implantable microfluidic ion pump system that can deliver large amounts of drugs to the brain with a low voltage and exceptionally high on-off ratio. In preliminary *in vivo* experiments in rats, which were described recently in *Advanced Materials* (doi:10.1002/adma.201701217), the researchers showed that the device could effectively alter the state of the brain.

“It’s a hybrid technology between a convection-enhanced delivery device and an ion pump,” says study lead author George Malliaras of France’s École Nationale Supérieure des Mines, referring

to two approaches for localized cortical drug delivery. “Our main achievement was to take an ion pump device, which is very promising for drug delivery, and to make it practical.”

Convection-enhanced delivery devices, or CEDs, use high pressure to deliver drugs with intracranial needles or catheters. Though the fluid-delivery systems can bypass the blood-brain barrier and deliver high local drug concentrations, they increase the local pressure around the target area, potentially deforming tissue and causing neural damage. An alternative platform for cortical drug delivery is the organic electronic ion pump (OEIP), which transports ions from a source solution to a target solution (within the brain) through a selective ion bridge such as a polyelectrolyte film. Unlike CEDs, OEIPs use dry delivery—only the drug and not the solution is delivered—and do not require high pressure. However, because the ion bridge that connects the drug reservoir outside the body to the target in the skull is a centimeter long, OEIPs require voltages of tens of volts to deliver adequate amounts of drugs, leading to possible harmful electrolysis of the brain, Malliaras says.



Microfluidic ion pump system placed on the surface of a rat’s cortex. Image courtesy of George Malliaras/*Advanced Materials*.

To get around the limitation of OEIPs, Malliaras and his colleagues sought to combine a microfluidic system with an ion pump. The resulting microfluidic system would bring the drug molecules close to the delivery point, where they are pumped to the target area through small holes coated with ion bridge material. The microfluidic channel acts as a passive drug reservoir, and for fully implantable applications, this channel can be replenished as needed using a connected subcutaneous