

# RESEARCH HIGHLIGHTS: Perovskites

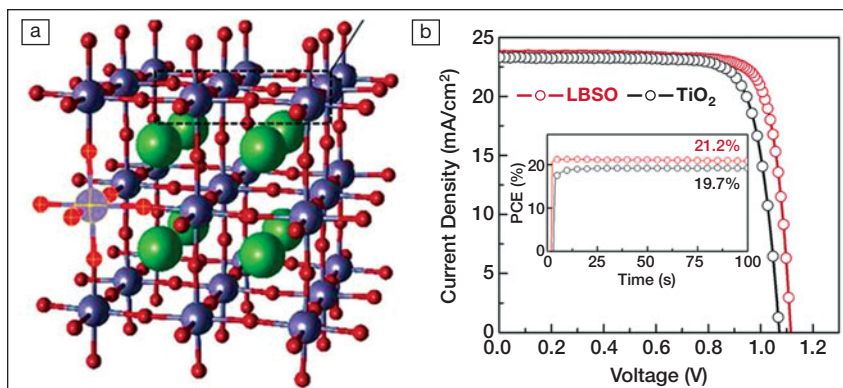
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Research on perovskites has progressed rapidly, with solar-cell efficiencies now at 22%, five times higher than those of the first cells reported in 2009. MRS Bulletin presents the impact of a selection of recent advances in this burgeoning field.

One of the biggest hurdles perovskite solar cells still face is their ability to weather moisture and ultraviolet rays.

Using a novel method to synthesize a lanthanum-doped barium tin oxide (LBSO) electrode, Korean researchers have made solar cells that are highly stable under light exposure and boast the highest reported efficiency for devices made of the perovskite methylammonium lead iodide ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ). Devices reported in a recent issue of *Science* (doi:10.1126/science.aam6620) demonstrate an efficiency of 21.2% and were stable for 1000 hours under full sun.

Efficient perovskite solar cells typically use titanium oxide as electron-transporting layers. However, titanium oxide reduces the stability of the devices under light. LBSO is an ideal replacement because it has a high electron-conveying ability and crystalline structure compatible with perovskites. But the material crystallizes at temperatures



(a) Structure of  $\text{BaSnO}_3$ . Green, gray, and red spheres indicate Ba, Sn, and O ions, respectively. (b) Perovskite solar-cell performance with lanthanum-doped barium tin oxide (LBSO). Adapted with permission from *Science* **356**, 167 (2017).

over  $1000^\circ\text{C}$ , making it hard to apply on glass and plastic surfaces.

Sang-Il Seok, at the Ulsan National Institute of Science and Technology, and his colleagues came up with a solution-based route to prepare a LBSO electrode at temperatures below  $300^\circ\text{C}$ . They first made a colloidal solution of

LBSO nanoparticles by the reaction of  $\text{BaCl}_2$ ,  $\text{SnCl}_2$ ,  $\text{La}(\text{NO}_3)_3$ , and  $\text{H}_2\text{O}_2$  in an  $\text{NH}_4\text{OH}$  aqueous solution at  $50^\circ\text{C}$ . LBSO perovskite crystals developed from the colloidal solution, which the researchers coated on a fluorine-doped tin oxide substrate to create the electrode.

A research team led by Zachary Holman of Arizona State University and Michael McGehee of Stanford University has made tandem perovskite/silicon solar cells with a record-high efficiency of 26.3% that are also highly stable.

Silicon/perovskite tandem cells typically contain perovskite layers deposited on top of crystalline silicon. They suffer from low stability as well as unwanted

light absorption in the top window layer through which light enters the solar cell. This light absorption reduces efficiency, so the window layer needs to be highly transparent. Indium tin oxide (ITO) is the ideal transparent electrode used in displays and solar cells, but the sputtering method used to deposit it can damage perovskite layers.

As reported recently in *Nature Energy* (doi:10.1038/nenergy.2017.9), the re-

searchers used a bottom silicon cell tuned to absorb infrared light. The top cell was made of the perovskite cesium formamidinium lead halide  $[\text{Cs}_{0.17}\text{FA}_{0.83}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3]$ . This stable perovskite allows researchers to deposit a tin oxide buffer layer, on top of which they could sputter-deposit an ITO electrode. The performance of the highly efficient devices did not degrade for more than 1000 hours of testing at  $85^\circ\text{C}$  and 85% relative humidity.



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  $\text{PbI}_2$  in a *N*-methyl-2-pyrrolidinone: *N,N*-dimethylformamide solvent and added an excess of methylammonium chloride.

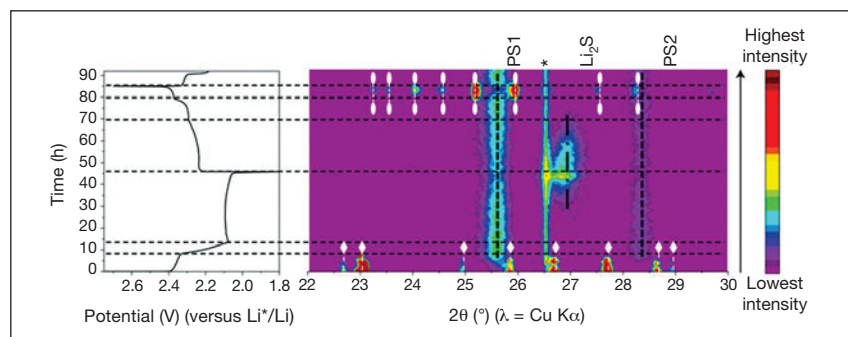
The ink can be deposited on a substrate using blade coating, an easily scalable processing method used to make large-area films on rigid or flexible surfaces in which a blade spreads liquid on a moving substrate. Instead of seconds, the precursor ink film can be processed for up to eight minutes. Further, it only needs a minute of heat treatment. All of this would be attractive for manufacturing. The researchers used the process to make  $1.2 \text{ cm}^2$  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 Avillevieille 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.  $\text{Li}_2\text{S}$  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 capacitance over time, and