In another *Nature Energy* article (doi: 10.1038/s41560-019-0466-3), a team lead by Hairen Tan of Nanjing University presented a different way to suppress tin oxidation in tin-lead perovskite layers. Their "simple and effective strategy" is to add metallic tin powder to the precursor solution from which perovskite films are made.

In the precursor, the species Sn^{2+} oxidizes to Sn^{4+}. But the metallic tin reduces the Sn^{4+} back to Sn^{2+}, the researchers found. They filtered out the leftover metallic tin granules before making a perovskite film. "By using this strategy, we are able to reduce the Sn vacancies inside the grains and thereby achieve a long carrier-diffusion length of 3 µm in mixed Pb-Sn perovskite films," they wrote.

The resulting tin-lead perovskite films have electronic quality comparable to high-quality lead-based perovskites. This, in turn, yielded tin-lead perovskite solar cells, with the highest reported power-conversion efficiency of 21.1%. Tandem cells made with these narrow-bandgap devices have a certified 24.8% efficiency for small-area devices (0.049 cm^2) and 22.1% for large-area devices (1.05 cm^2). The tandem devices retained 90% of their performance following 463 hours of operation at the maximum power point under full 1-sun illumination.

While most efforts on perovskite solar cells have focused on methylammonium lead trihalide perovskites, with bandgaps of 1.55 eV or higher, formamidinium-lead-iodide ($FAPbI_3$)-based systems, with their slightly narrower bandgap, have the potential to give more efficient photovoltaic devices.

The material's drawback is that within 10 days at room temperature, it transforms from a black phase to a yellow phase—which has trigonal versus hexagonal crystal symmetry, respectively—that has a wider bandgap. In a recent *Science* article (doi:10.1126/science.aay7044), researchers reported a method to stabilize the trigonal phase to make efficient, stable $FAPbI_3$ solar cells.

In the past, others have tried to stabilize $FAPbI_3$ by mixing in cations and anions such as methylammonium, cesium, and bromine. But these additives can also widen the bandgap and reduce stability. Sang Il Seok and his colleagues at the Ulsan National Institute of Science and Technology made highly efficient and stable perovskite solar cells by adding methylenediammonium dichloride ($MDACl_2$) to the a-$FAPbI_3$. The device had a certified efficiency of 23.7% and maintained over 90% of that initial efficiency after 600 hours of operation under full sunlight. Even unencapsulated devices exhibited better thermal and humidity stability over a control device in which $FAPbI_3$ was stabilized by $MAPbBr_3$.

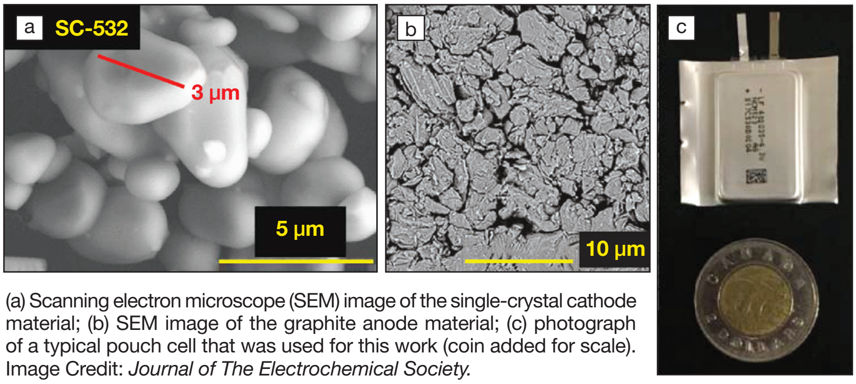
Energy Focus

High-performance, long-lasting battery comes with test protocol

Electric automobiles are becoming more popular and more common on the roads each year. These cars are viable because their battery banks store enough energy to facilitate daily commutes. They also deliver steady day-to-day performance and do not degrade rapidly. However, everyday commutes that are short and intermittent rarely tap the full capacities of these batteries. As long-haul trucks and driverless taxis transition from gasoline to electric power, their constant run time will have an adverse impact on the longevity of their batteries. Furthermore, hot and cold environments also affect the operational capabilities of electric vehicles. There is, therefore, a significant drive to deliver "beyond-lithium" cell chemistries for the next generation of batteries. The aforementioned host of dynamic variables presents a formidable challenge for these efforts: what is the most reliable protocol to evaluate these cells and, over a viable laboratory-scale test process, assess expected lifetime and failure mechanisms that accurately apply to real-life batteries that operate for several years?

A research group from the Department of Physics and Atmospheric Sciences and Department of Chemistry at Dalhousie University recently reported a lithium-ion cell chemistry design with excellent longevity. Their resulting battery design, which uses finely tuned electrode and electrolyte designs, also withstood temperature extremes, allowed fast charging, and was durable enough to power an electric vehicle for over 1 million miles. The group published their findings and methodology in a recent issue of the *Journal of The Electrochemical Society* (doi:10.1149/2.0981913jes).

A crucial component of the success of Jeff Dahn and his colleagues was the design of the cathode electrode in the battery cell. A single-crystal electrode composed of a lithium nickel manganese cobalt oxide yielded the highest and most durable



(a) Scanning electron microscope (SEM) image of the single-crystal cathode material; (b) SEM image of the graphite anode material; (c) photograph of a typical pouch cell that was used for this work (coin added for scale). Image Credit: *Journal of The Electrochemical Society.*

capacities. A carefully designed electrolyte that used an organic lithium salt, a blend of three organic solvents, and novel stabilizing agents acted as an essential partner to this electrode and ensured its durability over thousands of charge and discharge cycles. This stable system delivered a 795-Wh/L stack energy density and performed at high efficiencies over 3700 cycles at 20°C and 40°C. The unique design of the cathode ensured that the electrodes never cracked or effused active material.

Georgia Institute of Technology professor Gleb Yushin, who is unaffiliated with this research effort, assessed the impact of the work: “Development of longer lasting batteries [is] critical for both autonomous electric mobility and clean energy grid. Revealing key contributions to cell degradation, as demonstrated by this excellent work and others, enable materials scientists to fine-tune both electrode particles and electrolytes to overcome the current Li-ion limitations. In the near future, I expect new anode and cathode chemistries beyond graphite and NMC [nickel manganese cobalt] will push the limits of energy density versus cycle life to new heights.”

The researchers validated the longevity of their cells against comparable commercial cells and replicated expected operating conditions. The team stored the cells in temperature-controlled ovens for over a year and periodically cycled them to assess their thermal stabilities. Battery testing cycled the energy-storage modules at different rates and combined electrochemistry information with changes in volume (due to aging-induced generation of gas in the cells) and characterization of electrodes at different time points. The researchers meticulously documented their test methods and ensured that researchers could easily replicate these results or build upon them in follow-up efforts. Many of the tested cells are—to this day—still cycling in the Dalhousie University laboratories, and readers are encouraged to contact the research team and inquire about the current operating status.

Boris Dyatkin

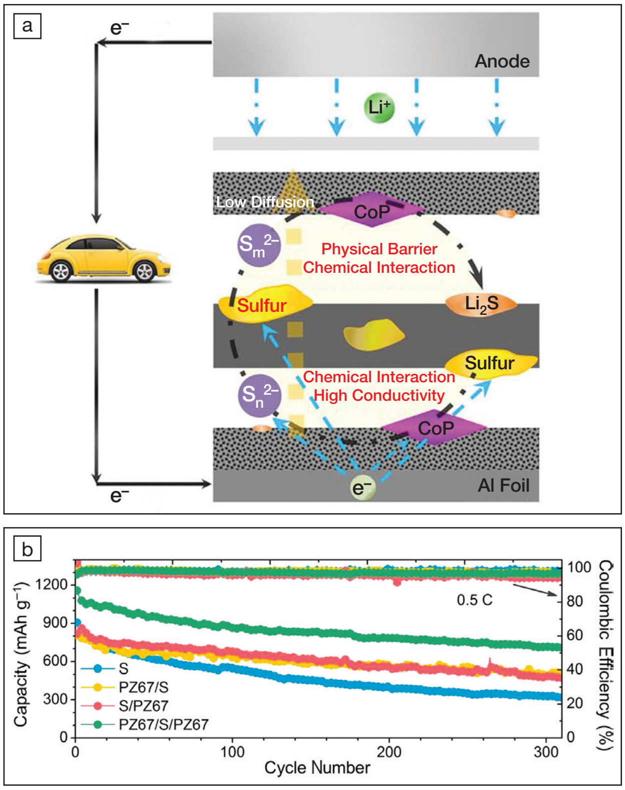
ENERGY FOCUS

Metal–organic-framework-derived “sandwiches” enhance longevity of Li-S batteries

Rechargeable lithium-sulfur (Li-S) batteries with elemental sulfur and lithium metal as cathode and anode, respectively, are promising electrochemical energy-storage devices with energy densities 3–5 times higher than those of rechargeable Li-ion batteries. However, the practicality of Li-S batteries is significantly compromised by their short lifetimes that are mainly associated with polysulfides, the intermediate products formed during cycling. Once formed, these electrolyte-soluble species diffuse to the Li metal anodes and deposit as Li_2S on the Li surface. The deposition passivates Li and reduces the concentration of Li^+ available for electricity storage. Therefore, developing methods to prevent polysulfide diffusion to Li anodes is crucial for addressing the implementation challenge for the Li-S battery.

In *APL Materials* (doi:10.1063/1.5122819), Bo Wang and co-workers of the Beijing Institute of Technology, China, describe a cobalt phosphide/porous carbon composite (PZ67) that prevents the leaking of polysulfides into the electrolyte. The PZ67 composite results in Li-S batteries with a high capacity (a metric for quantifying electricity-storage capability) that goes beyond 300 charge-discharge cycles.

According to the first author, Xing Gao, the purpose of this work was to utilize polar compounds and porous carbon networks to trap polysulfides. To realize this goal, the researchers selected ZIF-67, a type of cobalt-containing metal–organic framework (MOF), as a starting material. MOFs are crystalline coordination compounds consisting of metal ions or clusters and organic ligands. Through thermal annealing and phosphidation by NaH_2PO_4 under N_2 atmosphere, ZIF-67 was converted to cobalt monophosphide (CoP) nanoparticles wrapped with N-doped mesoporous carbon matrices.



(a) Scheme showing that the PZ67 “sandwich” prevents polysulfides (S_m^{2-} and S_n^{2-}) from diffusing to Li anodes. (b) Cycling stability of Li-S batteries with various cathodes: bare sulfur (S), PZ67-supported sulfur (PZ67/S), PZ67-covered sulfur (S/PZ67), and PZ67-sandwiched sulfur (PZ67/S/PZ67). CoP, cobalt monophosphide. Credit: *APL Materials*.

The PZ67 composite functioned as a “cage” to confine polysulfides near sulfur. Specifically, sulfur was sandwiched between two pieces of PZ67 but remained accessible to Li^+ through