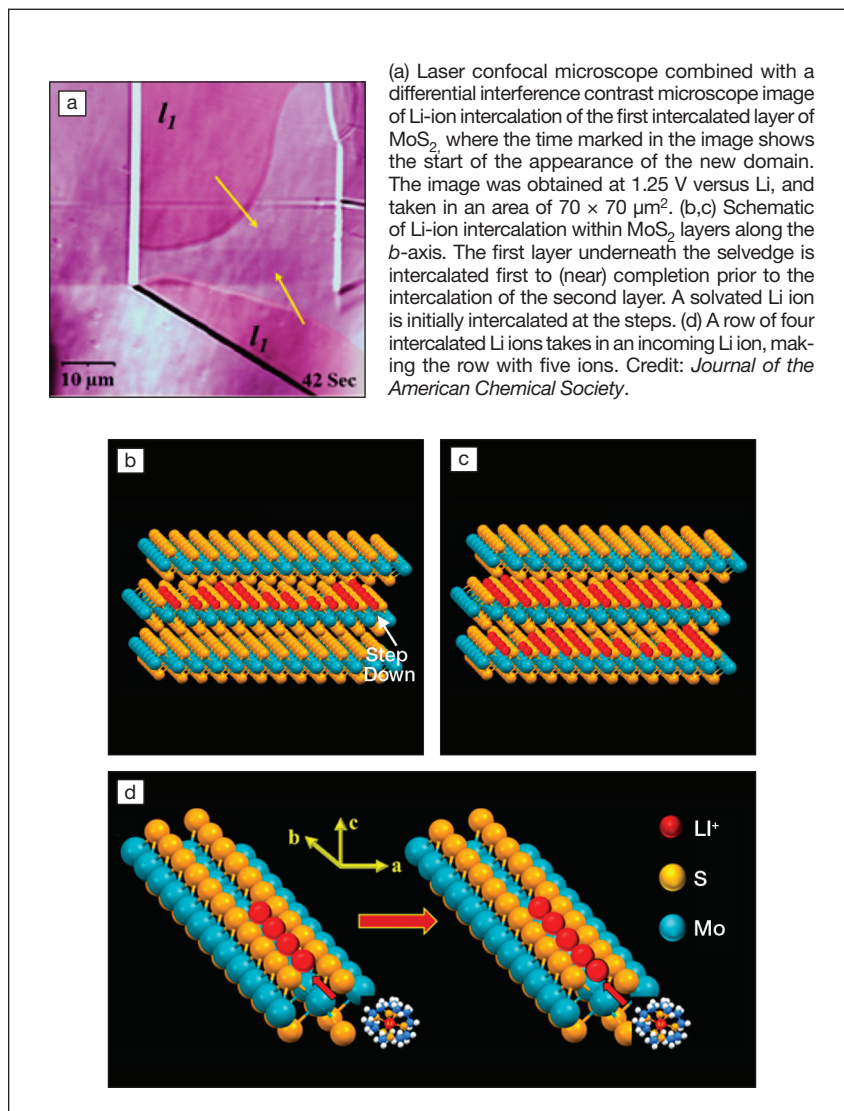


Energy Focus
Lithium-ion intercalation visualized *in situ* with new atomic-scale imaging technique

Intercalation in rechargeable lithium-ion batteries—the process where lithium ions pack themselves in between adjacent two-dimensional layers of an electrode material—is integral to the operation of the batteries. The complete dynamics of this process have not yet been visualized. M. Azhagurajan from Tohoku University, Y.-G. Kim from the California Institute of Technology, and their colleagues have now succeeded in this goal, as reported in their article published recently in the *Journal of the American Chemical Society* (doi:10.1021/jacs.5b11849).

The major technological advance achieved by the team was the development of a combined laser confocal microscopy-differential interference microscopy (LCM-DIM) imaging technique, which enabled single atomic step heights down to tenths of nanometers to be resolved. Using this technique, the researchers examined the intercalation and deintercalation of lithium within MoS₂ layers, recording and analyzing contrasts in the images. They found that intercalation occurs layer by layer in a step-wise manner; beginning at the layer's edge, a lithium ion enters between MoS₂ layers. The ion then accommodates a second ion by shifting one unit cell toward the interior of the layer. These two intercalated ions then shift one unit cell toward the interior to accommodate a third ion. This process continues until a layer of MoS₂ is almost completely intercalated with Li ions before intercalation in the subsequent layer begins. Deintercalation proceeds in a similar way.

The layer-by-layer process of intercalation and deintercalation gives rise to a distinct phase separation between



the intercalated and non-intercalated regions. Using the LCM-DIM *in situ* dynamic visualization technique, the team was able to see the intercalated region expand as a front moving through the material, much like a layer of water expands to cover a smooth surface. With application of greater current, net-like disruptions occurred in the layer surface.

These reticular regions later developed into cracks in the MoS₂ surface.

The LCM-DIM opens the door to detailed analysis of atomic-scale surface phenomena that are accompanied by changes in optical properties, potentially ushering in novel discoveries and advances in battery technology.

Antonio Cruz

Glassy poly(lactide) toughened with diblock copolymer micelles

Growing environmental concerns are calling for nondegradable petroleum-derived plastics to be replaced

with biodegradable, more sustainable options. Poly(L-lactide) (PLLA), a product of polymerization of L,L-lactide and a different form of poly(lactide) (PLA) by virtue of its chirality, is one of the many viable alternatives with high tensile strength and high elastic modulus,

but its intrinsically brittle characteristic must be overcome for applications requiring toughness, impact resistance, and optical clarity. A research group with the Center for Sustainable Polymers at the University of Minnesota have now successfully toughened PLLA by



uniformly dispersing short cylindrical micelles of a low-molecular-weight poly(ethylene oxide)-*b*-poly(butylene oxide) (PEO-PBO) diblock in commercial high-molecular-weight glassy PLLA. Introduction of these micelles into the PLLA results in a greater than tenfold increase in tensile toughness and notched Izod impact strength.

“Despite standard polymer physics, the attempt was to try and toughen PLA by creating the same type of nanoscale micelles that the group has been investigating for years in epoxy resins. This finding has the potential to be a facile and economical way to toughen PLA and perhaps produce low-density porous films,” says chief scientist Frank Bates.

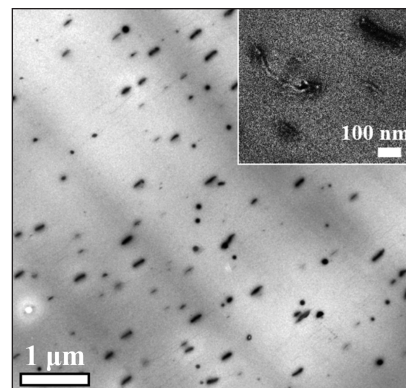
As reported in a recent issue of *ACS Macro Letters* (doi:10.1021/acsmacrolett.6b00063), Tuoqi Li, a graduate student in the group, synthesized a series of PEO-PBO diblock copolymers (a polymer with distinct blocks of monomers PEO and PBO grafted together to form a single copolymer chain), identified as EB1–3, as well as a PLLA-PBO diblock, identified as LB, by anionic polymerization with fixed composition but with varying total molecular weight. Blends of PLLA and both the diblock PLLA copolymers were then prepared by solvent and melt blending routes, followed by rapid cooling and aging for two days prior to characterization.

The resulting blend, identified as EB1/PLLA, showed a dispersion of the EB1 copolymer into small micelle-like

particles as shown in the figure. In general, increasing the overall molecular weight of the EB additives in PLLA led to coarser dispersions and larger domain sizes than those expected from the assembly of individual micelles. The blend prepared using EB1 exhibited the greatest improvement relative to neat PLLA with a 1300% increase in tensile toughness and a 2500% increase in strain at break. By adding 1.25 wt% and 5 wt% EB1 to the PLLA, the notched Izod impact strength (measured by impacting the specimen by an arm from a height, and measuring the amount of energy absorbed by the sample) could be improved by 600% and 1500%, respectively.

“This is an exciting advance by Bates and co-workers that shows how diblock polyether additives can have a profound influence on toughness and impact strength without degrading other properties,” explains Geoffrey Coates, an expert in defined structure polymers from Cornell University. He further says, “These additives have great potential to create poly(lactides) that have performance characteristics that match their already impressive environmental attributes.”

The favorable enthalpic dispersion of EB1 into bulk PLLA as a micelle microstructure was attributed to a negative Flory–Huggins interaction parameter, which means that the mixing is of an exothermic nature. Study of the tensile specimens before and after deformation suggested that the improved performance



Transmission electron microscope image of 5 wt% EB/PLLA blend showing, in the inset, the micelle structure at a higher magnification. Credit: *ACS Macro Letters*.

derives from the formation of micron and submicron holes, which are caused by cavitation of the rubbery core micelles. Along with this kind of cavitation, micromechanical mechanisms of crazing and shear yielding are believed to produce a synergistic toughening effect in the PLLA-EB1 blends.

This work represents a significant step toward developing a low-cost approach for toughening sustainable glassy PLLA materials based on a facile processing route. The controlled cavitation and void formation observed offers a new method for producing low-density porous materials with a host of potential applications. Future research would entail a more comprehensive study of the toughening mechanisms for the series of EB diblocks.

Rachana Acharya

Energy Focus

Carbon nanotubes improve radiation resistance of aluminum

The limited operating lifetimes of nuclear structural materials is due to embrittlement and porosity that occur in these materials under long-term radiation exposure near a reactor core. Carbon nanotube (CNT)-reinforced aluminum composite materials provide a possible solution to this problem. The addition of small quantities of CNTs to aluminum dramatically improves the material's

irradiation tolerance, suggesting potential applications in nuclear reactors, nuclear waste containers, nuclear batteries, and spacecraft. The dispersion of multi-walled carbon nanotubes in a metal matrix effectively mitigates radiation damage through additional internal interfaces for self-healing of radiation defects, and improves the mechanical properties by inhibiting dislocation propagation.

In a recent issue of *Nano Energy* (doi:10.1016/j.nanoen.2016.01.019), a research team led by Ju Li from the Departments of Nuclear Science

Engineering and of Materials Science Engineering at the Massachusetts Institute of Technology investigated the basic materials science of an aluminum/CNT composite. “The key technology of our research is the dispersion of the CNTs inside metal grains,” says Kang Pyo So, the lead author of this work. These CNTs facilitate the recombination of atomic-level defects, such as vacancies, interstitials, and dislocation loops, and may provide pathways for releasing helium instead of trapping helium along grain boundaries to cause embrittlement. CNTs transform