

**Glassy lithium forms superior metal anode for rechargeable Li batteries**

Lithium metal is theoretically the best anode material for Li-based batteries. However, it is notorious for irregular growth upon repeated battery operation, thus limiting its practical relevance. Accordingly, graphite anodes that exhibit smaller but sustained performance have been used in traditional Li-ion batteries for the past four decades. The pursuit of more energy-dense batteries for the next-generation electrification challenges has redirected researchers' attention to lithium anodes. The latest advances in experimental imaging and computational capabilities have started to provide new insights into the underlying fundamental mechanisms accounting for the idiosyncrasies of electrochemically grown lithium.

Recent research reported in *Nature Materials* (doi:10.1038/s41563-020-0729-1) explores the initial stages of lithium electrodeposition in liquid electrolytes – mimicking the behavior of Li-metal anodes in batteries. The study finds that the crystallinity of the freshly grown lithium strongly affects its operation. The work was carried out by Boryann Liaw, Y. Shirley Meng, and colleagues from Idaho National

Laboratory, University of California, San Diego, and Pacific Northwest National Laboratory. To track the initial stages of nucleation and growth, at every current density (i.e., growth rate), electrodeposition was carried out for progressively longer times and the resultant growth structures were analyzed using cryogenic transmission electron microscopy to assess crystallinity of the new phase and scanning electron microscopy (SEM) to visualize the growth morphology.

The nucleated phase (very early times) is found to be amorphous. As the deposited clusters grow, they gradually transition to an ordered (crystalline) phase. Such a disorder–order phase transition is found to be strongly sensitive to the growth rate where faster deposition (i.e., higher current) leads to more crystalline deposits. Reactive molecular dynamics (MD) simulations were performed to probe the origins of such a phase transition, revealing that large initial nuclei were crystalline while smaller ones were amorphous. Thus, higher currents lead to larger initial nuclei that grow as crystalline deposits, while smaller ones at low currents grow as a disordered amorphous phase.

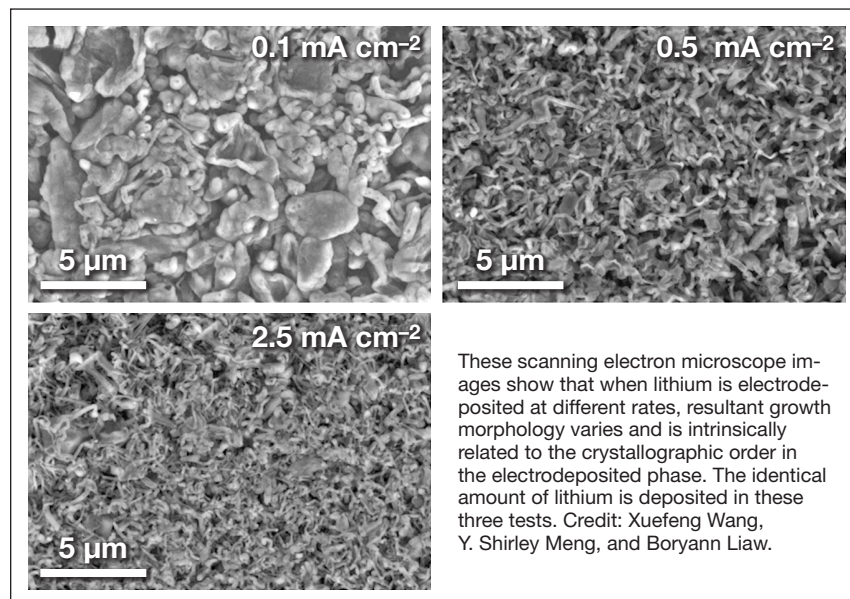
Since a crystalline phase grows to conform to the crystal shape (thermodynamic Wulff shape), sharp growth features are observed. On the other hand, amorphous

nuclei grow in a relatively uniform fashion. Such differences are apparent in SEM images of growth morphology. Classical nucleation theory does not account for the disorder–order phase transition that is important to describe the differences in the growth morphologies. Similar current-dependent disorder-to-order behavior was observed when the researchers electrodeposited sodium, potassium, magnesium, and zinc—other metal anodes of interest.

Visualizing the interface structure is a challenging aspect, in part because the lithium surface is tricky to preserve going from battery to the imaging station. The high reactivity of lithium forms new phases at the interface of interest as soon as the electrodes are extracted from cells and come in contact with the ambient. The cryogenic technique developed by Meng's group cleverly circumvents this and lets one observe relevant growth features. Liaw points out that the researchers were initially surprised by the glassy deposits because one would expect the post-nucleation growth to transition to the crystalline state. MD calculations helped identify the underlying “long incubation times” that meta-stabilized the glassy phase.

This study reveals that the amorphous lithium leads to desired growth morphology. To further test this hypothesis, the researchers examined electrodeposition at identical currents but using two different electrolytes. It is observed that the electrolyte that gives more amorphous deposits also exhibits superior performance and reversibility, further bolstering the importance of amorphous growth.

While discussing this study, Jürgen Janek and Thorben Krauskopf from Justus-Liebig-Universität Giessen, Germany (not related to the work), mention that controlling the evolution of nanostructure and microstructure of lithium is the key to reversible metal anodes. They are optimistic about the new opportunities this work promises via tailoring morphology of the electrochemical growth. They suggest that this work demonstrates a poorly understood coupling between reaction kinetics and growth that unlike classical nucleation theory predictions, exhibits larger cluster sizes for faster growths. A possible explanation





is the role of surface diffusion (*Energy Environ. Sci.*, doi:10.1039/C8EE01448E) that occurs concurrently with reaction and growth. Other exploratory opportunities are to scale up this mechanism to any current of interest and explore whether the

amorphous growth is a strict criterion for homogeneous deposition.

The research team is excited about examining the regimes of glassy electrochemical growth to enable anodes made of other metals. Given its correlation to small current

densities, (i.e., growth rate per unit area), one interesting possibility is to examine three-dimensional structures whose higher area-to-volume ratio can facilitate desired glassy growth for the same total current.

**Aashutosh Mistry**

### Self-intercalation forms covalently bonded 2D transition-metal chalcogenide layers

A research team led by Kian Ping Loh and Stephen J. Pennycook of the National University of Singapore, as well as Xin Luo of Sun Yat-sen University, report a new class of metal chalcogenides in their article published in *Nature* (doi:10.1038/s41586-020-2241-9). These materials are transition-metal dichalcogenide bilayers sandwiching metal atoms covalently.

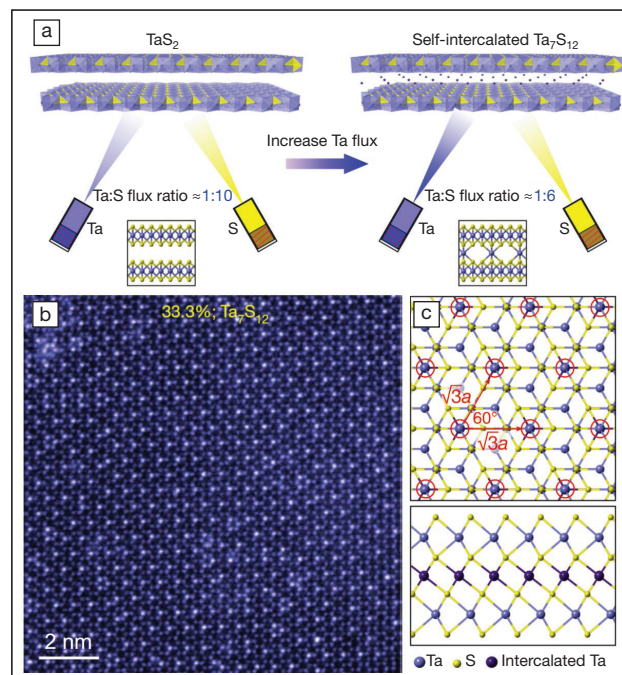
The layered structure of metal dichalcogenides enables the synthesis of novel materials. Typically, two-dimensional (2D) metal dichalcogenides are composed of nanosheets stacked together, in analogy to graphene. Adjacent layers are held together via weak van der Waals forces. The interlayer spaces can host guest species, including atoms and ions. Previous work focused primarily on introducing foreign ions or atoms within a single metal-chalcogenide layer, “but somehow, previous researchers missed considering the situation when the same metal atoms sit in between two layers,” says Xiaoxu Zhao, the lead author. The researchers decided to step into this unexplored area.

The research team modified the synthesis protocols involving molecular beam epitaxy (MBE) for synthesizing metal dichalcogenides. MBE is a gas-phase technique for growing highly uniform and crystalline thin films. The key to the synthesis of a new family of metal chalcogenides is to enhance the concentration of gaseous metal precursors intentionally. During the thin-film deposition, the additional metal atoms reside in the interstitial space between the as-formed metal dichalcogenide monolayers and formed covalent bonds with neighboring layers. For example,

increasing the Ta:S flux ratio from 1:10 (which formed conventional metal dichalcogenide,  $\text{TaS}_2$ ) to 1:6 resulted in Ta-intercalated tantalum disulfide,  $\text{Ta}_7\text{S}_{12}$ . Changing the flux ratio was found to tune the stoichiometry to obtain other compounds, for example,  $\text{Ta}_9\text{S}_{16}$  and  $\text{Ta}_{10}\text{S}_{16}$ . Additionally, this strategy is also applicable to chemical vapor deposition, another common synthesis technique of metal dichalcogenides.

In some cases, the newly synthesized metal chalcogenides possess magnetic properties that their corresponding monolayer counterparts lack. The intercalated metal atoms located in the interstitial sites in the interlayer space can transfer electrons to the host layers, altering the electronic structure of the metal chalcogenides, rendering different magnetic behaviors. For instance, the newly synthesized  $\text{Ta}_7\text{S}_{12}$  is ferromagnetic, whereas its parental compound,  $\text{TaS}_2$ , is non-ferromagnetic.

Babak Anasori of Indiana University–Purdue University Indianapolis believes that “adding covalent bonds between the flakes of transition-metal dichalcogenides will lead to new compounds with large available compositional space while keeping the thickness at ultrathin nanometer levels. This strategy might



Self-intercalation in  $\text{TaS}_2$  crystals. (a) Scheme of the synthesis method, (b) atomic-resolution scanning electron microscopy–annular dark-field image, and (c) atomic model of  $\text{Ta}_7\text{S}_{12}$ . The bright dots in (b) and red circles in (c) highlight the location of intercalated Ta atoms. Credit: *Nature*.

[unveil] novel properties, including room-temperature, ambient-stable two-dimensional ferromagnets.” Anasori was not involved in this study.

Significantly, density functional theory predicts that besides Ta and S, transition metals of V, Cr, Mn, and Te, along with VI-A elements of S, Se, and Te, are feasible elements constituting the self-intercalated chalcogenides. Zhao says, “Owing to the versatility in the composition control, it is possible to tune, in one class of materials, properties that can vary from ferromagnetic to non-ferromagnetic and spin-frustrated Kagome lattices. This discovery presents a rich landscape of ultrathin three-dimensional materials that await the further discovery of new properties.”

**Tianyu Liu**