

Transmission X-ray Microscope: A Powerful Tool for the Structural Analysis of Energy Materials

Understanding the electrochemical performance of energy materials through micro-structural analysis.

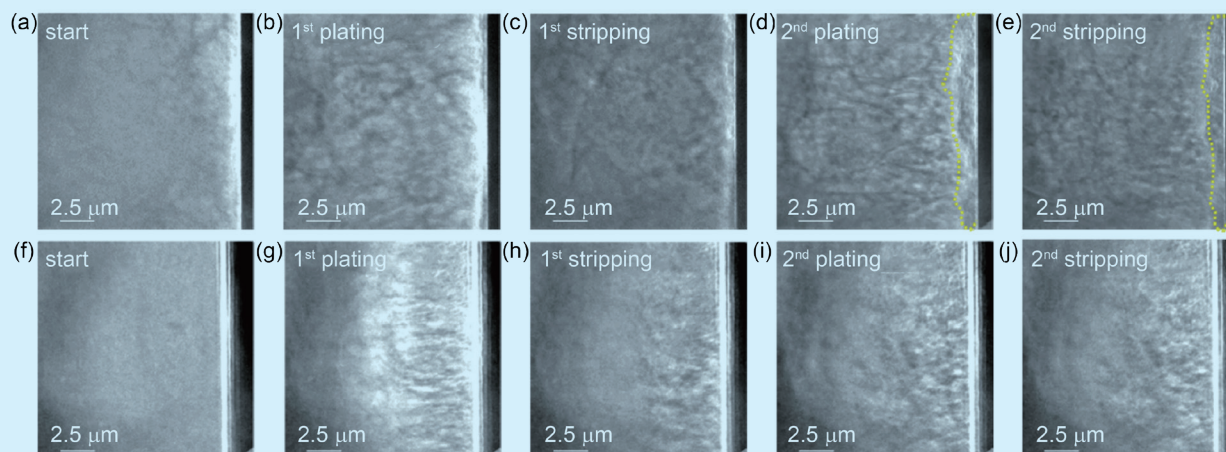


Fig. 1: *In operando* TXM lithium morphologies after charge (plating) and discharge (stripping) steps in $\text{Li}_2\text{S}||\text{Cu}$ (a–e) and $\text{LiFePO}_4||\text{Cu}$ (f–j) at 1.5 mA cm^{-2} . [Reproduced from Ref. 1]

Structural changes in energy materials during charging and discharging significantly affect their coulombic efficiency, cycle life, and overall stability. The synchrotron-based transmission X-ray microscope (TXM) employs a high-energy hard X-ray source, providing spatial resolutions down to 60 nm. Its penetrating capability allows for the observation of sub-micron structural changes of the material within a battery's complex layers, including those containing electrolytes. TXM's real-time and synchronized monitoring capabilities grant comprehensive insights into how different materials, electrolytes, and additives influence battery performance. This makes TXM an indispensable instrument in the field of energy materials research.

The research group led by Bing Joe Hwang from the National Taiwan University of Science and Technology recently employed a TXM at the beamline **TLS 01B1** to investigate the deposition patterns of lithium metal on electrodes during charge–discharge cycles of anode-free lithium-sulfur batteries (AFLSBs). Their study uncovered the fundamental origins of superior electrochemical performance behind these batteries.

The efficacy of lithium plating and stripping processes is vital for the performance of anode-free batteries. Notably, redox-active polysulfides (PS) have crucial effects on the development of lithium plating morphologies. *In operando* TXM, used during live charge and discharge cycles of $\text{Li}_2\text{S}||\text{Cu}$ and $\text{LiFePO}_4||\text{Cu}$ anode-free batteries, captures the evolving states of lithium plating.¹ **Figure 1** features TXM images showcasing the plating morphologies within the $\text{Li}_2\text{S}||\text{Cu}$ and $\text{LiFePO}_4||\text{Cu}$ cells. Initially, the contrast between copper and electrolyte is evident in the TXM images of both batteries (**Figs. 1(a) and 1(f)**). After the first plating in the $\text{Li}_2\text{S}||\text{Cu}$ AFLSB cell, a dense lithium layer emerges, as seen in **Fig. 1(b)**, which is indicative of the PS's role in stabilizing lithium deposition. Conversely, the lithium in the $\text{LiFePO}_4||\text{Cu}$ cell displays a mossy morphology (**Fig. 1(g)**). Upon the second plating cycle, a compact layer of lithium forms closer to the copper interface in the $\text{Li}_2\text{S}||\text{Cu}$ AFLSB cell (depicted in yellow in **Fig. 1(d)**), a phenomenon not seen in the $\text{LiFePO}_4||\text{Cu}$ cell. These findings affirm the role of PS species in regulating the morphology of lithium plating in all-solid-state lithium-sulfur batteries. The *in operando* TXM observations highlight the importance of PS species in the stable deposition of lithium.

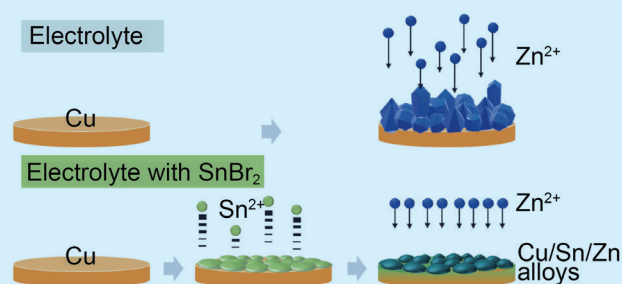


Fig. 2: Schematic illustration of the working mechanism of electrolyte without and with SnBr_2 . [Reproduced from Ref. 2]

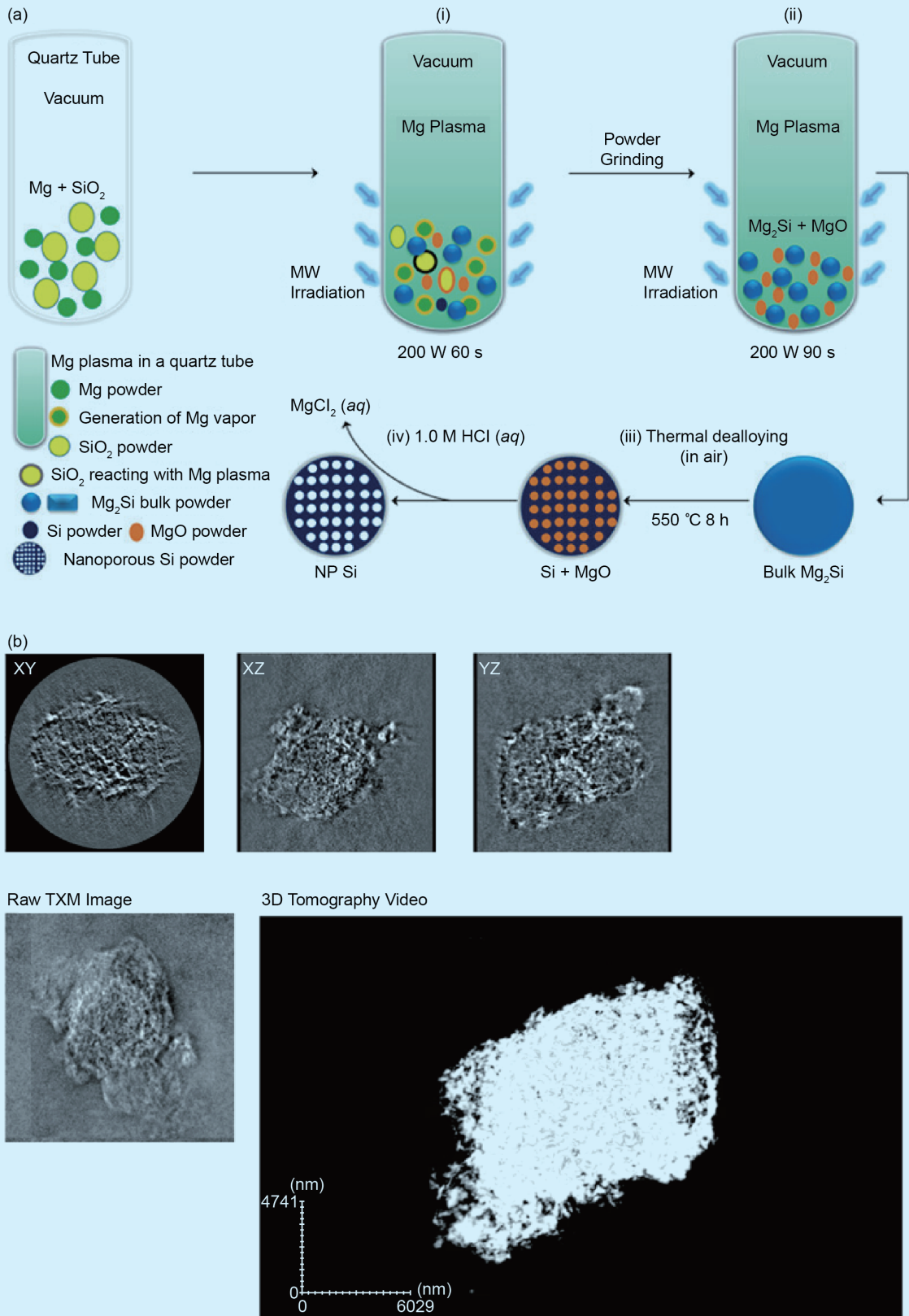


Fig. 3: (a) Schematic of the MIMP-assisted synthesis of NP-Si from SiO₂. (b) Transmission X-ray microscopy directly reinforces this representation of the 3D NP microstructure. [Reproduced from Ref. 3]

In addition, Hwang's team has been championing a groundbreaking anode-free rechargeable aqueous hybrid battery design noted for its exceptional safety, eco-friendliness, and affordability. This innovative architecture is initiated through the *in situ* deposition of tin onto the surface of a copper current collector, with the electrolyte serving solely as the source of zinc ions.² The *in operando* TXM observations enhance our understanding of the mechanisms behind zinc and tin plating and stripping on the copper substrate.

In operando TXM imaging has the capability to monitor interfacial phenomena and changes in morphology during the processes of zinc deposition and removal. Notably, the findings indicate that the additive-free electrolyte cannot establish a stable coating. By contrast, adding SnBr₂ to the electrolyte promotes the formation of a copper–tin alloy, leading to effective nucleation, thus achieving a more uniform and consistent layer of zinc deposition. The resulting formation of a uniform and compact layer of zinc implies that the initial nucleation of tin plays a crucial role in ensuring the evenness and smoothness of the zinc layer. The distinct plateau, indicative of Cu/Sn/Zn alloy formation, signifies improved nucleation and homogeneity in zinc deposition. As shown in Fig. 2, the tin layer aids in creating a smooth, uniform, dense, and dendrite-free zinc layer on the copper, a process enhanced by favorable conditions provided by alloy formation. The formation of the copper–tin alloy stabilizes the zinc plating and removal within the anode-free aqueous hybrid battery, achieving an average coulombic efficiency of approximately 99.1%. This is in stark contrast to the 97.6% efficiency of the electrolyte without any additives. Utilizing an electrolyte enriched with SnBr₂, the capacity retention rate after 100 charging and discharging cycles increases significantly to 35.2%, a substantial increase from the mere 7.8% observed in the absence of additives. Thus, the addition of SnBr₂ significantly improves zinc deposition and removal processes by encouraging the formation of a Cu/Sn/Zn alloy inside the battery, resulting in a more stable cycle life free from dendritic zinc growth.

Moreover, in the realm of battery research, analysis of energy materials' three-dimensional structure is crucial for improving our understanding of battery performance. Recently, Duncan H. Gregory from the University of Glasgow (United Kingdom) and Yan-Gu Lin from the NSRRC collaborated, utilizing the TXM to investigate these aspects. Their research focused on the three-dimensional characterization of a novel nanoporous silicon (NP-Si) material, which shows promise in replacing conventional graphite anodes in lithium-ion batteries, potentially improving their performance. The viability of NP-Si as a sustainable material is closely related to its production process, which traditionally relies on methods that are harmful to the environment. To address this, the collaborative team developed a more environmentally friendly production technique that efficiently converts SiO₂ into Mg₂Si using low-powered microwaves in conjunction with magnesium plasma. The microwave-induced metal plasma (MIMP) method (see Fig. 3(a)) produces a three-dimensional NP-Si structure, characterized using the TXM (as shown in Fig. 3(b)), that is particularly well-suited for use as an anode in batteries.

In summary, the use of synchrotron-based transmission X-ray microscopy for analyzing the three-dimensional tomographies of energy materials, coupled with the observation of structural changes during *in situ/in operando* electrochemical reactions, provides a crucial visualization of how material structures affect battery performance. This valuable insight has the potential to expedite the development and performance evaluation of new energy materials. Consequently, the TXM has established itself as an essential and irreplaceable tool in the field of energy materials development and research. (Reported by Chun-Chieh Wang)

This report features the work of Bing-Joe Hwang and his collaborators published in ACS Energy Lett. **8**, 2817 (2023) and *Electrochim. Acta* **443**, 141883 (2023), and the work of Duncan H. Gregory and his collaborators published in *ACS Appl. Mater. Interface* **15**, 36076 (2023).

TLS 01B1 X-ray Microscopy

- TXM
- Energy Materials, Materials Science, Environmental and Earth Sciences, Physics

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