Towards Quantitative Liquid Phase Electrochemistry for Understanding Electrochemical Processes

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Background incl. aims
Liquid phase transmission electron microscopy (LPTEM) has emerged as a powerful tool, presenting enormous potential for understanding the electrochemical processes behind electrolysis, batteries, and other technologies [1]. However, obtaining high-resolution structural and chemical information during these electrochemical processes remains a challenge due to the issue of liquid thickness. While utilizing a monolithic MEMS-based nanoreactor with integrated electrodes can be a potential solution, it too faces limitations from an electrochemical perspective. To ensure proper ion conduction to mirror processes occurring in macroscopic cells, LPTEM studies require a thicker liquid layer, which directly contradicts the need for high-resolution information. On the other hand, obtaining high-resolution information through post-mortem studies, by disassembling a typical two-chip nanoreactor, too is not a viable solution due to possible changes due to absence of the native liquid environment. Furthermore, ideally high-resolution information is required at different stages of in situ experiments. These necessitate the ability to dynamically control the liquid thickness.
novel method that enables high-resolution and analytical electron microscopy studies within a liquid flow cell [2].

Methods
Smart micro electrical mechanical systems (MEMS) and holder designs have enabled us to control liquid flow and thickness, allowing us to create a stable and reproducible environment that is ideal for investigating the electrochemical processes of interest [2,3]. In particular thanks to the on-chip flow capability, the liquid in the field of view can be efficiently reduced by flowing gas, which is termed “purging” [4]. This purging method enables the acquisition of high-resolution TEM images, chemical composition and valence analysis through energy-dispersive X-ray spectroscopy (EDX) mapping and electron energy-loss spectroscopy (EELS). In addition, the purging approach is both reversible and reproducible, which therefore enables the alternation between a thick and a thin liquid configuration. This provide us the necessary dynamic control over the liquid thickness to perform the electrochemical experiments in a thick liquid configuration and then perform anlytical studies including 4D STEM at the thin liquid configuration to enable the best resolution without changing the state of the sample. This coupled with simple image processing that has allowed us to extract 3D information from the in-situ image series and a step towards live 4D STEM provides the pathway to developing new and more efficient energy technologies.

Results
Dendrite growth during cycling is one severe problem to harm durability and safety of energy applications, so many efforts have been studied to inhibit the dendrite growth. One example case is aqueous zinc (Zn) based battery chemistry, including redox flow battery, which has recently generated significant interest as an alternative battery technology for stationary applications beyond Li-ion batteries. The main driving force is the high volumetric capacity of aqueous zinc batteries, low cost, safety, and abundance of Zn metal. Despite these

advantages, alongside electrode passivation, anode shape change, and H2 evolution, the problems of Zn dendrite growth cause premature battery failure and safety hazards, severely limiting the progress and further commercial exploitation of aqueous Zn batteries. Direct visualization of dendrites under operando conditions can lead to an in-depth understanding and the development of the most effective mitigation routes toward achieving a compact plating and smooth stripping of Zn during battery cycling, which is a prerequisite for battery safety, longevity, and viability. Thus we apply the developed method for dynamic control of liquid thickness and image processing to gain 3D growth along with crystallographic orientation information of the Zn deposits during electrodeposition using 0.1 M ZnSO4.
Figure 1. Showcase dendrite formation and extracted 3D information from the in-situ image series.

Conclusion

The 3D visualization of electrodeposition at the nanoscale enabled us to study how different electrolyte additives affect growth across all three planes (XY, YZ, and XZ) and thus establish a workflow that researchers can utilize to optimize electrolytes to promote compact deposition and mitigate unwanted features like dendritic growth for Zn and other battery chemistries and electrodeposition processes in general.

Figure Caption

Figure 1: Investigation of Zn dendritic growth during plating in static 0.1M ZnSO4. (a-c) STEM images obtained at 7th, 8th and 9th seconds. (d) The plated Zn volume vs. time. (e-g) Processed images show the Zn dendritic growth between 7-8, 8-9, and 9-10 seconds. A color map on (g) represents the thickness [µm] at that second.

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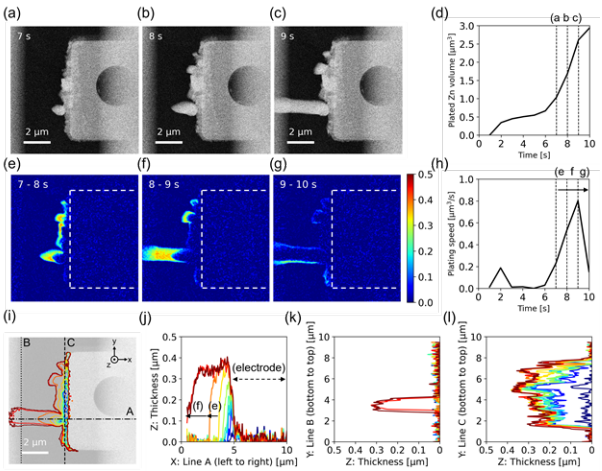
Graphic:



Keywords:

liquid phase TEM, 4DSTEM, 3D

Reference:

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