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Metal Electroplating/Stripping and 4D STEM Analysis Revealed by Liquid Phase Transmission Electron Microscopy

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Aqueous zinc ion and metal-based batteries have attracted much attention towards the development of an alternative electrochemical energy storage technology beyond lithium ion batteries [1]. There are several advantages of metal-based batteries, including high volumetric capacity (~8000 mAh/L), low anode potential (~0.7 V vs. SHE), safety and electrode abundance. However, the problem of metallic dendrite growth during cycling can cause battery short circuit failure, which can result in safety hazards and severely limit the progress and further commercialization [2, 3]. To this end, direct visualization of dendrite evolution under operando conditions is a prerequisite for battery safety and longevity. Among the many operando/in situ techniques, the use of liquid phase transmission electron microscopy (LPTEM) [4] has been very effective in enabling a more detailed understanding of metal plating and stripping, where the ability to locally probe and visualize the key processes governing the dendrite formation. However, it remains challenging to perform high resolution and analytical electron microscopy studies in a liquid cell, especially under liquid flow conditions.

In this work, we use LPTEM [5, 6] to directly visualize the electroplating and stripping of metals on micro-electrodes of dedicated MEMS (micro-electro-mechanical system) chips at the nanoscale. By comparing the plating/stripping under different chemical and/or electrochemical environments, including static or flow electrolyte conditions and varying current densities, we show how metal dendrites can be effectively controlled on electrochemical cycling of the battery, as revealed by our operando LPTEM observations. In addition, we recently developed a liquid purging approach, which is based on the DENSsolutions unique Liquid Supply System and the on-chip liquid flow capability (Figure 1). This approach enables one to perform 4D STEM electron diffraction analysis on the plating (Figure 2). Following the experimental results, the growth of zinc dendrites can be effectively mitigated and directly minimized by flowing electrolyte into the cell and adjusting the current density, thus, providing new insights into the aqueous metal battery's chemistry and the pathways for further optimization.

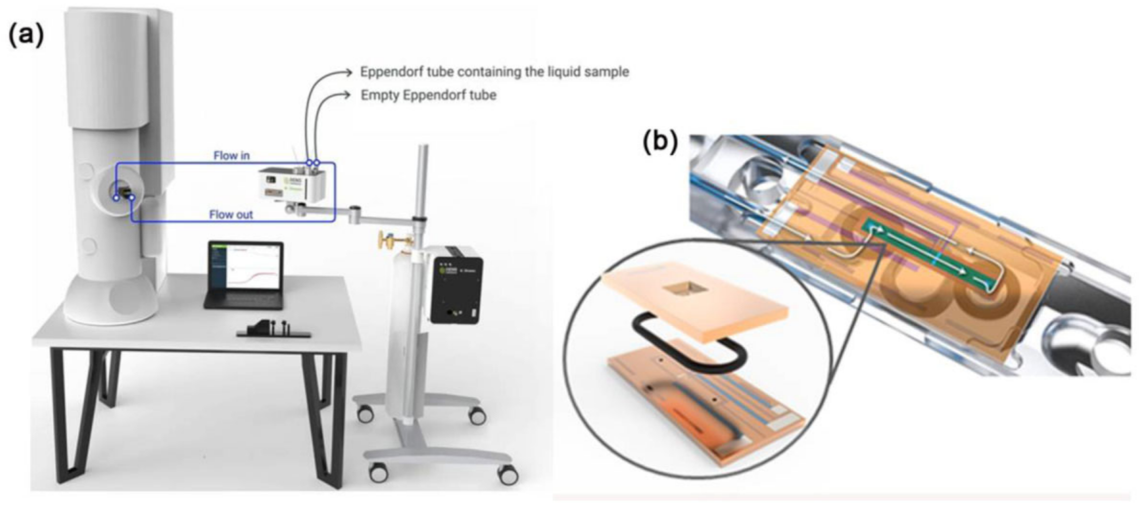

Fig. 1. (a) A schematic representation of an in situ liquid experimental setup showing the in situ TEM holder inserted in a TEM (left), the Liquid Supply System with integrated pressure-based pumps (right), a gas bottle to drive the liquid (*Flow in*) from the sample reservoir to the TEM holder (blue line). There is also an empty reservoir connected to the outlet of the holder (*Flow out*) to collect the liquid sample after being observed in the TEM. (b) A render of the Stream holder with an inserted liquid biasing Nano-Cell showing the flow path of the liquid, with the top chip made transparent for clarity. The inset shows the full Nano-Cell including the top and bottom Nano-Chips.

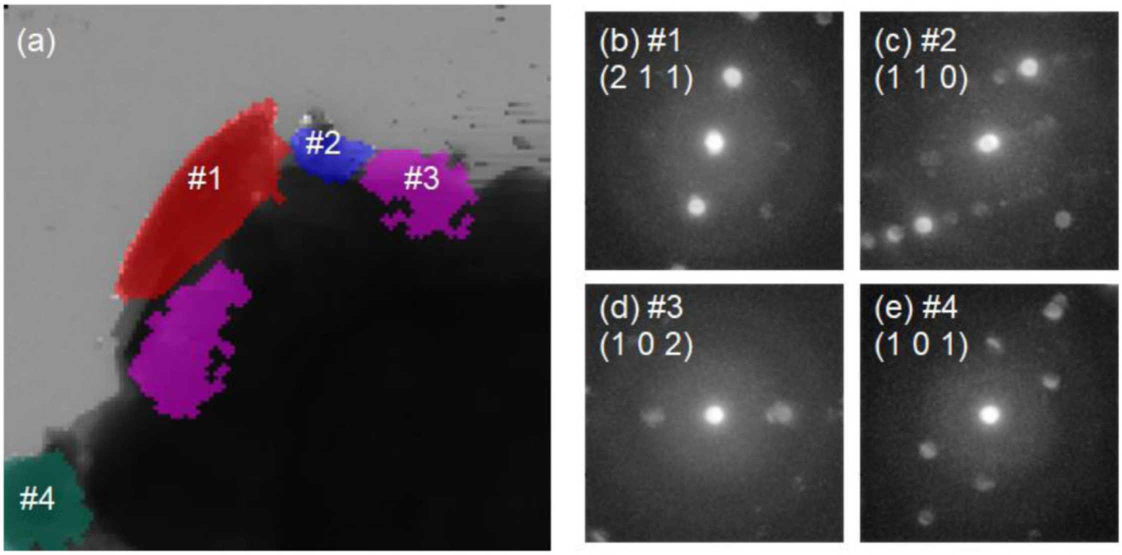

Fig. 2. (a) Orientation-mapped STEM image of deposited zinc in liquid by 4D STEM data analysis. (b-e) Reconstructed electron diffraction patterns corresponding to each mapped region.

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