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TUTORIAL

A beginner's guide to quantitative *in-situ* liquidphase transmission electron microscopy for electrochemistry

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Abstract

Liquid-phase transmission electron microscopy (LPTEM) bridges the critical gap between bulk electrochemical measurements and nanoscale structural evolution. It offers insight into mechanisms such as metal plating and stripping in batteries, catalyst degradation in fuel cells, and surface reconstruction of electrocatalysts during CO_2 reduction. However, standard LPTEM is frequently hindered by undefined mass transport and severe beam-induced artifacts. This tutorial outlines a rigorous methodology to transition LPTEM from a passive observation tool to a quantitative analytical technique. It details the design of experiments that utilize controlled flow to define the chemical environment, discusses critical material choices, specifically the replacement of standard platinum microelectrodes with carbon-based microelectrodes to minimize catalytic side reactions and improve electron transparency. Furthermore, it provides a workflow for data acquisition and post-processing, demonstrating how to extract volumetric growth kinetics, particle size distributions, and facet evolution metrics from noisy S/TEM videos. Finally, we address common pitfalls, particularly the management of gas evolution during electrochemistry and distinguishing electrochemical nucleation from beam-induced reduction. This guide equips researchers to obtain reproducible, artifact-free, and quantifiable data at the solid-liquid interface during liquid phase electrochemistry.

Glossary

LPTEM	Liquid Phase Transmission Electron Microscopy; a technique for imaging samples in liquid encapsulated between electron-transparent windows (usually SiN_x or graphene) within a high-vacuum TEM column.
MEMS	Micro-Electro-Mechanical Systems; in the present context, silicon-based microchips used to encapsulate liquid, pattern microelectrodes, and integrate heaters, allowing electrochemistry at different temperatures.
Radiolysis	The dissociation of the liquid electrolyte by the high-energy electron beam, creating reactive species that can artificially drive reduction or oxidation.
Mass Transport	The movement of chemical species (ions, reactants) to and from the electrode interface. In LPTEM, this must be actively controlled to mimic macroscopic device operation.
HAADF-STEM	High-Angle Annular Dark Field Scanning Transmission Electron Microscopy; an imaging mode where contrast is proportional to the atomic number and sample thickness.
4D STEM	A scanning technique that records a diffraction pattern at every pixel, enabling the crystallographic mapping of materials and strain analysis at the nanoscale.

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1. Introduction

Electrochemical energy technologies, from high-energy-density metal-anode batteries to proton exchange membrane fuel cells and CO_2 electrolyzers, rely on interfacial processes that occur at the nanoscale. Mechanisms such as dendritic nucleation during metal plating, solid electrolyte interphase formation, the coarsening of platinum nanoparticles in fuel cells, or the restructuring of copper nanocubes during CO_2 reduction dictate device performance and failure. While traditional electrochemical methods (cyclic voltammetry (CV), impedance spectroscopy) provide ensemble-averaged global data, they cannot resolve discrete local events. *In-situ* liquid phase transmission electron microscopy (LPTEM) has emerged as the technique capable of visualizing these dynamics, even at different temperatures, in real-time with sub-nanometer resolution [1]–[8].

However, the transition from a bulk reactor to a microscopic liquid cell is fraught with challenges. Conventional 'static' or 'diffusion-based' liquid cells often suffer from rapid depletion of reactants, and accumulation of beam-induced by-products as well as electrochemically generated bubbles. If the mass transport inside the nanoreactor cannot be directly controlled, the local environment would become fundamentally different from a realistic device, which would often lead to unrepresentative results. For example, in batteries, rapid depletion of ions and ppm-level additives would artificially promote dendritic growth, failing to reflect the true effectiveness of electrolyte engineering. In fuel cells, this diffusion-limited confinement would prevent ion washout, leading to artificial re-deposition of dissolved catalyst ions that would stabilize catalysts and obscure true degradation rates.

To obtain physically meaningful data, we must engineer the micro-environment [9]. This requires: (a) active control of mass transport via microfluidics to define diffusion boundary layers and flush beam-induced depositions [10]; (b) the selection of microelectrodes that are electrochemically inert and electron transparent, serving effectively as working electrode and/ or current collector [11]; and (c) real-time monitoring of the pseudo-reference potential to account for drift [12]. Finally, successful LPTEM requires a shift from qualitative interpretation to quantitative image analysis [13]. This tutorial, drawing upon over a decade of hands-on experience, provides an entry-level workflow guiding the newcomer through this transition, focusing on the engineering of the cell, the execution of artifact-free experiments, and the extraction of kinetics. We highly recommend consulting the broader foundational literature for more sophisticated methodological approaches.

2. Design

The design of a quantitative LPTEM experiment rests on three engineering pillars: fluidic architecture, microelectrode selection, and liquid thickness management. Furthermore, modern MEMS architectures allow the integration of micro-heaters, enabling temperature-dependent kinetic studies [5, 15].

Fluidic Architecture: Static cells, typically containing less than 1 nL of electrolyte, are insufficient for quantitative electrochemistry. In battery research, active flow (1–5 μl min^{-1}) is mandatory to maintain a constant concentration of metal ions, preventing complete ion depletion (the 'sand time' effect). Crucially, flow ensures that ppm-level additives are continuously replenished; otherwise, the experiment reverts to 'additive-free' behavior due to adsorption depletion. For gas-evolving reactions like CO_2 reduction, standard syringe pumps lack innate pressure control. To ensure bubble-free viewing, researchers must either integrate a back-pressure regulator at the outlet to statically pressurize the cell (e.g. $>$1.5 bar) and increase gas solubility, or utilize advanced MEMS designs optimized for rapid bubble evacuation.

Electrode Material: Standard platinum (Pt) microelectrodes present significant limitations in LPTEM. Pt has a high atomic number, making it opaque to electrons and masking nucleation events. Furthermore, Pt is catalytically active for hydrogen evolution, generating bubbles in aqueous electrolytes that disrupt imaging. Carbon-based (glassy carbon or graphite) microelectrodes are preferred as they not only mimic the carbon supports used in real devices, but they are highly transparent, allowing higher resolution imaging on the support material. Other exploratory microelectrodes should be looked into [11, 16].

Liquid Thickness: A fundamental trade-off exists between electrochemical reliability and imaging resolution. 'Realistic' bulk-like behavior requires a thick liquid layer for unhindered ion transport, whereas

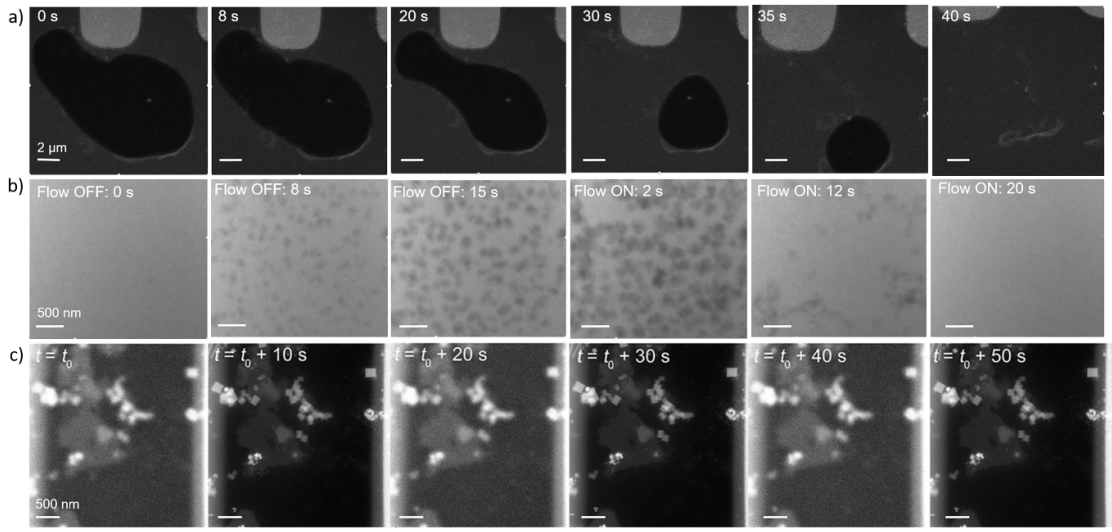


Figure 1. Mitigation of common artifacts in quantitative LPTEM electrochemistry. (a) Dissolution of electrochemically generated bubbles by increasing cell pressure. (b) Removal of beam-induced deposition via continuous electrolyte flow. Reproduced from [10]. © IOP Publishing Ltd. All rights reserved. (c) Dynamic control of electrolyte thickness by regulating the differential pressure between the inlet and outlet. Reproduced with permission from [14]. © Oxford University Press on behalf of The Japanese Society of Microscopy. All rights reserved.

high-resolution demands thin layers to minimize electron scattering. This gap can be bridged by active pressure regulation. By controlling the differential pressure between the inlet and outlet, this allows the experiment to cycle between a 'thick' mode for reliable electrochemical operation and a 'thin' mode for high-resolution snapshots, 4D STEM or EDS/ EELS acquisition [14].

Figure 1 shows mitigation of some of the common artifacts in LPTEM electrochemistry.
Outlook: While the modular two-chip assembly remains standard, the field is exploring monolithic electrochemical liquid cells. Building upon earlier foundational monolithic architectures [17], recent advancements overcome fabrication complexities to incorporate microelectrodes directly into the nanochannels. These designs eliminate alignment errors and mitigate window bulging for atomic-resolution studies, though managing the active mass transport required for quantitative electrochemistry in these confined geometries remains a challenge.

3. Experiment

Successful execution requires a strict protocol to ensure electrochemical validity and TEM safety.

Preparation and Assembly: Chips must be plasma-cleaned (Ar/O_2) immediately before assembly. This along with cleanliness ensures hydrophilicity, resulting a better wetting behavior of the chip with the aqueous electrolyte. Never insert a liquid cell directly into the TEM. Perform a vacuum leak check in a dedicated pumping station first. Always filter the electrolyte to ensure no clogging of the tubing. For gas-consuming reactions like CO_2 reduction, saturate the electrolyte with gas for at least 30 min prior to loading.

Establishing the Baseline: Introduce electrolyte at a moderate flow (1–5 μl min^{-1}) and monitor the open circuit potential (OCP). A stable OCP indicates a continuous liquid layer. A fluctuating or 'noisy' OCP is often a signature of a micro-bubble trapped over the reference electrode or intermittent contact.

To perform quantitative studies, it is crucial to separate beam-induced effects. Step 1: Active Baseline Tuning: Before applying potential, systematically adjust the average flow velocity and STEM dwell time. Fast flows and short dwell times promote a reductive environment (growth). Conversely, slow flows and longer dwell times accumulate secondary radiolysis products, promoting an oxidative environment (etching). Step 2: Achieving Net-Zero: Fine-tune these parameters until beam-induced particle growth and dissolution reach a net-zero balance. This establishes optimal conditions to minimize irradiation effects.

Step 3: Operando Testing: Apply the external electrochemical bias to investigate true electrochemical phenomena [18].

Electrochemical Protocols: Start with performing CV and observe reproducibility of the CV curves. Due to the inherent instability of on-chip pseudo-references, redox peaks will not match literature values. Always post-calibrate the potential internally by aligning observed *in-situ* features (e.g. redox onsets) with macroscale CV data. Choose current (or potential) value from the CV curve for further experiments.

- Battery Additive Screening: Run a control experiment with pure electrolyte first, then, without disassembling, switch the inlet to the additive-containing electrolyte. Use chronoamperometry (CA) to compare nucleation density and morphology under identical conditions.
- Fuel Cell AST: Apply square wave potential cycling to simulate start-stop conditions and image at intervals (e.g. every 100 cycles) to track particle coarsening.
- CO_2 reduction: Apply constant negative potentials and observe catalyst restructuring.

4. Data

The output of an LPTEM experiment is a dense 4D dataset (x, y, z-intensity, time) often reaching tens to hundreds of gigabytes. Converting this raw stream into kinetic data is the analytical core of the study [13].

Acquisition Strategy. STEM mode with a high-angle annular dark field (HAADF) detector is recommended, as Z-contrast facilitates interpretation. Balance temporal resolution with dose; fast scanning (e.g. $<$0.1 s/frame) is necessary for nucleation, while slower interval imaging (e.g. 1 frame min^{-1}) is preferred for degradation studies.

Quantitative Processing Workflow. When an experiment is successfully conducted within an actively tuned net-zero regime, the primary objective is to isolate genuine dynamic electrochemical volume changes from the static cell environment. Transitioning from raw, drift-prone STEM images to quantitative data involves a systematic workflow:

1. Drift correction: Apply rigid body alignment (StackReg/TurboReg) to correct sample drift.
2. Denoising: Apply a Gaussian or non-local means filter to raw images to suppress Poisson noise without blurring edges.
3. Background subtraction: Subtract the static background (the initial reference STEM image, I_0) from the target frame (I_n). Next, apply a threshold (T) to isolate the dynamically plated material. This mathematical isolation of true electrochemical phenomena is represented by $P_n = \{G(I_n)—G(I_0)\} > T$, where P_n is the final processed image and G is the Gaussian filter.

Quantification. The following metrics are the most common quantitative outputs extracted from LPTEM videos:

Volumetric Growth Kinetics: By summing the pixel intensities of the segmented deposit, one can plot 'Deposited Volume vs Time'. The derivative of this curve yields the instantaneous volumetric current, which can be compared to the potentiostat's recorded current to determine the local faradaic efficiency.

Growth Directionality (*Anisotropy*): To quantify the effect of additives, one can analyze the intensity gradient vectors at the growth front. A narrow angular distribution of these vectors indicates highly directional (dendritic) growth, while a broad distribution reveals the isotropic 'leveling' effect often desired in battery plating.

Shape Descriptors: For catalyst degradation or restructuring (e.g. in CO_2 reduction), tracking geometric descriptors such as circularity or aspect ratio quantifies the morphological transition from initial cubic or faceted shapes to spherical, degraded particles.

Figure 2 shows a simple data processing approach for quantitative outputs.

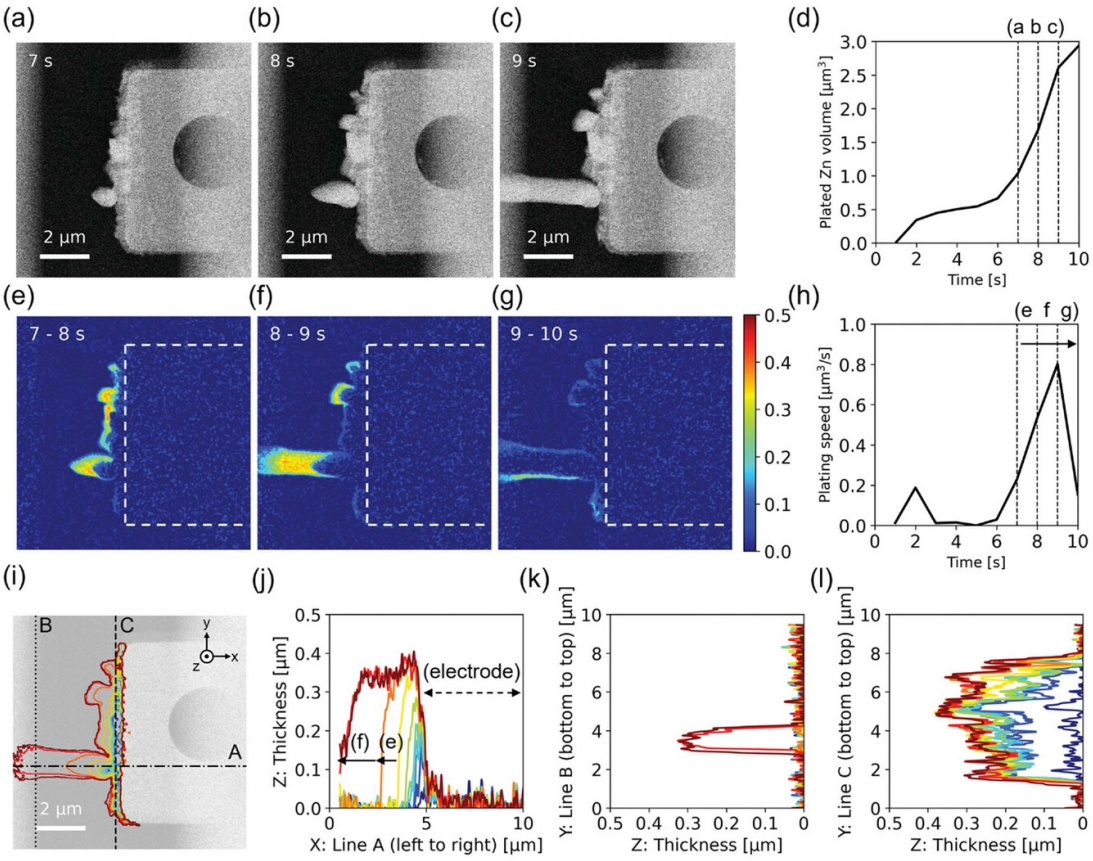


Figure 2. Extraction of electrochemical metrics from *in-situ* LPTEM video. (a)–(c) Time-resolved HAADF-STEM frames capturing the growth of a zinc dendrite at 1-second intervals. (d) Calculated volumetric growth kinetics (volume vs. time) derived from pixel intensity, which serves as a proxy for the local electrochemical current. (e)–(g) False-color thickness maps visualizing the 3D mass distribution of the deposit. (h) Instantaneous plating speed derived from the volumetric data, reflecting the real-time reaction rate. (i)–(l) Spatial thickness profiling (along lines A, B, and C) used to quantify dendrite morphology and local mass transport conditions. Reproduced from [13]. CC BY 4.0.

5. Practical considerations

Distinguishing genuine electrochemical phenomena from artifacts is the primary challenge for newcomers.

1. **Limitation of Net-Zero Tuning.** It must be noted that achieving a net-zero balance does not mean radiolytic species are completely absent. Enhanced growth or dissolution due to the presence of these species must still be considered, especially if the liquid composition or beam flux changes over time. Continuous visual monitoring of the structures is required to ensure the net-zero baseline holds throughout the experiment [18].
2. **Instability of the Pseudo-Reference Electrode.** The standard on-chip Pt pseudo-reference functions as a mixed-potential electrode, making it sensitive to the local chemical environment rather than defining a stable thermodynamic standard. In LPTEM, beam-induced radiolysis products and confined-volume pH swings cause this potential to drift unpredictably. Consequently, potentials recorded in this manner are often arbitrary. To obtain rigorous data, researchers should ideally use holder designs that either integrate a true reference electrode directly at the holder or establish an ionic bridge to a standard reference electrode located outside the microscope [12, 19, 20].
3. **Window Bulging and Path Length Uncertainty.** Quantitative STEM relies on the linear relationship between pixel intensity and mass-thickness. However, silicon nitride windows bulge outwards due to the pressure differential between the liquid and the high-vacuum column. This creates a 'pillow effect' where the liquid thickness varies significantly from the edge to the center. This non-uniform background complicates background subtraction and introduces errors in volumetric calculations. To mitigate this, map the liquid thickness using EELS (log-ratio method) prior to electrochemistry.

4. **Gas Evolution and Micro-Bubble Management.** To minimize imaging disruptions, thoroughly pre-saturate the electrolyte off-chip before loading. During operation, apply brief flow surges via the syringe pump to mechanically flush out pinned bubbles, or utilize the aforementioned back-pressure regulation to dissolve them if the fluidic setup permits.

5. **Strict Electron Dose Minimization.** Even with baseline tuning, minimizing radiolysis requires operating at the lowest possible dose rate. To further prevent degradation, researchers should keep the beam blanked during extended electrochemical protocols, un-blanking only briefly at regular intervals to acquire necessary snapshots.

6. Summary

In-situ LPTEM is a transformative technique, but only when rigorously controlled. It must not be treated as a plug and play system. By replacing static environments with controlled microfluidics, understanding beam effect, replacing interfering Pt electrodes with carbon microelectrodes, and replacing qualitative observation with quantitative image processing, we can eliminate the 'black box'. This approach allows us to measure the fundamental kinetics of battery failure, fuel cell degradation, and CO_2 catalyst restructuring with the same rigor as bulk electrochemistry, but with the sub-nanometer resolution.

Data availability statement

No new data were created or analysed in this study.

Highly recommended/Further reading

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Conceptualization (lead), Writing – original draft (lead), Writing – review & editing (lead)

Rüdiger-A Eichel
Funding acquisition (lead), Writing – review & editing (supporting)

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