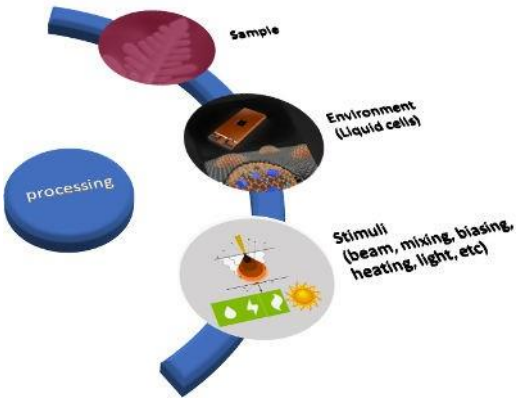
OBSERVATION AND CHARACTERIZATION OF COPPER ELECTRODEPOSITION IN LIQUID PHASE ELECTRON MICROSCOPY

INTRODUCTION

The ability to observe liquid processes with nanoscale spatial resolution or higher has been a wish ever since the early days of electron microscopy. Liquid-phase Transmission Electron Microscopy (LPTEM) is a technique that integrates liquid flow capabilities within microfabricated liquid cells, providing the means to study different processes in solution with sub-nanometer spatial resolution and sub-microsecond temporal resolution. Using this technique, it is now possible to visually study topics ranging from material science to life science[1,2]. Examples of measurements enabled by this technique are biomineralization processes[3], protein dynamics and structure[4,5], the influence of drugs on receptors in cancer cells[6], materials changes during the cycling of batteries[7,8], the growth of metallic nanoparticles or structures in liquid[7], and electrochemical processes such as metal deposition[9]. Metallic or alloy nanostructures show indeed benefits of increasing contact area with the reaction medium, and accelerating mass/ion transportation in chemical or electrochemical reactions. As the morphology, chemical composition, and crystallization in the nanostructures play important roles in determining their performance, direct observation of formation processes as well as in-situ characterization of nanostructure to monitor the evolution of structural parameters is crucial to yield materials that deliver optimized performance.



Nevertheless, current LPTEM methods usually lack appropriate fluidic control (e.g. diffusion-based approaches, limiting the control of the flow speed and direction in the region of interest) and suffer from undesired electron beam irradiation effects (e.g. deposition of unwanted beam induced species), resulting in limited analytical TEM approaches and irreproducible experimental results. To address this concern, DENSsolutions, in collaboration with Fluigent, implemented a LPTEM system employing pressure-based flow controllers, and a dedicated Nano-Cell design. This system ensures a constant and well defined flow on the sample area, and enables full control of liquid environment. As a result, the user is able to reliably measure the correlation between materials processing, structure, properties and performance, while observing real-time dynamics in liquid as a function of either heat or biasing.

There are several key advantages of this technique including:

- Control over liquid environment in a micro or nanoscale space
- Study dynamic processes in the liquid phase with nanoscale spatial resolution
- Determine the chemical composition in-situ
- Obtain electronic structure information

In this application note, we demonstrate the efficiency of this LPTEM system by performing controlled electrolyte injection and tuning the liquid thickness within the Nano-Cell. Cyclic voltammetry is used to study the electrodeposition, and to observe the growth and morphology evolution of Cu dendrites. Finally, microstructure and chemical composition of the obtained depositions are directly analyzed in the liquid phase by performing EDX (Energy-Dispersive X-ray Spectroscopy) mapping, and SAED (Selected Area Electron Diffraction).

MATERIALS AND METHODS

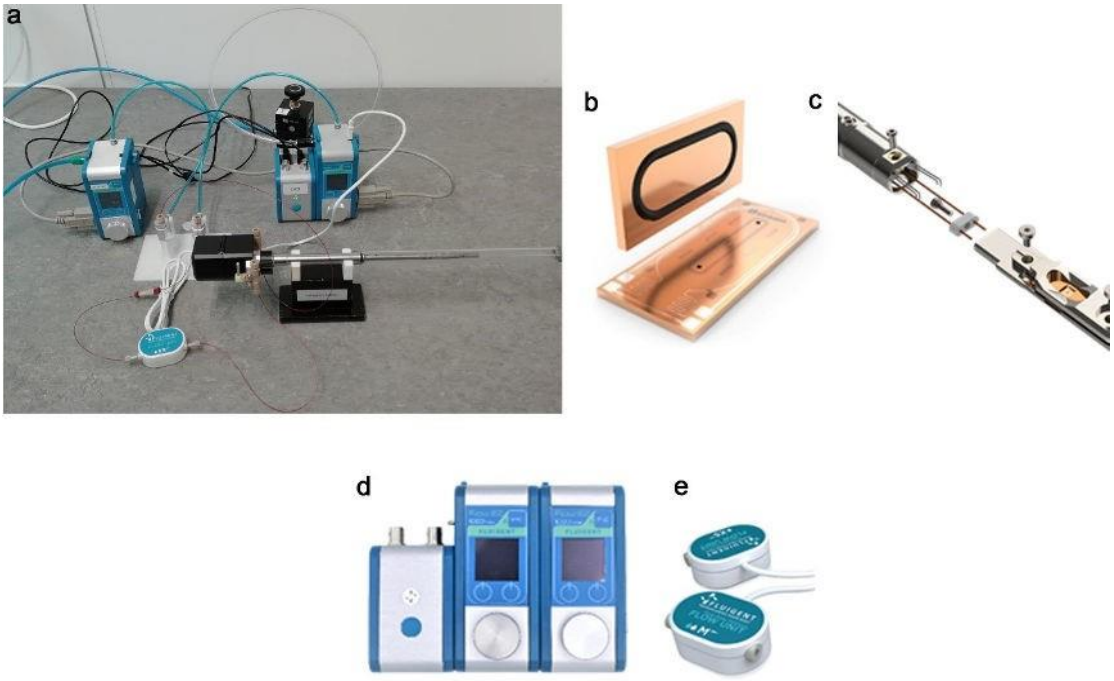


Figure 1. (a) Full setup of the system, consisting in the Stream Nano-Cell (b) placed within the TEM Sample Holder (c), The LineUp microfluidic flow controllers consisting in two Flow EZ and a LINK (d), and a Flow Unit XS (e). The flow rate can be locally controlled using the Flow EZ display or by linking the Flow EZ to a computer and using OxyGEN software.

I. Materials

Liquid cell

The Stream Nano-Cell is a an advanced flow cell for controlling liquid environment within the microscope, and includes the following features:

- Defined liquid channel and no dead volumes
- Pressurized inlet and outlet to accurately define pressure and flow rate, independently
- Drastically reduced bulging for easier imaging

Sample holder

The in situ TEM Sample Holder provides the platform for connecting the pressure-based flow controller to the Nano-Cell. The modular design allows for each vacuum component to be either cleaned or replaced which ensures each new experiment is free from cross-contamination. The highest precision fabrication techniques were used to machine the in situ TEM Sample Holder to perfectly fit the microscopes goniometer.

Microfluidic flow controller

The Flow EZ is the most advanced flow controller for pressure-based fluid control. It can be combined with a Flow Unit to control pressure or flow rate. It can be used without a PC. One Flow EZ 1000 mbar and one Flow EZ -800 mbar are used in the setup presented here. Note that it is also possible to go one step further by upgrading the flow controller to OEM, allowing to integrate this solution in a dedicated system while keeping the high-precision flow control provided by Fluigent.

Flow sensor

The Flow Unit is a flow sensor that allows real time flow rate measurement. By combining a Flow Unit with the Flow EZ, it is possible to switch from pressure control to flow rate control, allowing the generation of highly monodispersed droplets over a long period of time. One Flow Unit XS was used here.

OxyGEN software

Fluigent's OxyGEN software is a complete interface allowing one to control, monitor and automate Fluigent product line.

TEM

FEI Titan 80-300.

Liquid sample

$CuSO_4$ (20 mM) and KH_2PO_4 (10 mM) mixed aqueous solution.

II. Setting up the system

The Nano-cell relies on the dual-chip concept of sandwiching two MEMS devices to seal a miniaturized chamber. The two windows are aligned on top of each other in a cross-configuration, yielding a viewable area of 20 x 20 μm^2. The Nano-cell is assembled in its dedicated holder, which acts as the interface to the external electronics and the microfluidic flow controller. To control the pressure inside the Nano-cell, the pressures at both the inlet and outlet of the holder must be controlled. Therefore, two independent Flow EZ are used to set the pressure of the holder inlet and outlet tubing; over-pressure (pushing/infusing) on the inlet reservoir and under-pressure (pulling/withdrawing) on the outlet reservoir. Note that the TEM's vacuum pressure is not affected by these operations, as the windows physically separate the inside of the Nano-cell from the vacuum of the TEM. Where syringe pumps only push the liquid into the inlet, this system allows independent control of flow and pressure inside the Nano-cell. For example, by increasing the pressure difference between the inlet and outlet, the flow will increase. Keeping the pressure difference the same while lowering both pressures simultaneously will reduce the absolute pressure in the Nano-cell without a change in flow. The latter is especially beneficial to reduce the bulging of the windows, and consequently the thickness of the liquid layer. The absolute pressure in the liquid cell can here be varied from -200 mbar to 2000 mbar. Liquid was typically injected within the flow cell using a flow rate of 1,7 µL/min, the electrochemical potential window is -0.70 V - +0.30 V (vs. Pt) and the scan rate for cyclic voltammetry measurement is 50 mVs^{-1}. TEM analysis techniques such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), EDX mapping, and SAED, can be performed.

RESULTS

I. Control of the liquid flow and thickness within the microfluidic chamber

To demonstrate the high level of liquid control within the microfluidic chamber, the electrolyte (20 mM $CuSO_4$ and 10 mM KH_2PO_4 mixed aqueous solution) was flowed into the window area and subsequently evacuated using the system described in the "Materials & Methods" part of the application note. Figure 2 shows HAADF-STEM images of the window area of the Nano-Cell observed under different environmental conditions: (a) no liquid, (b) completely filled with liquid, (c) partially filled with liquid and (d) no liquid. This confirms that by regulating the driving force (i.e. absolute pressure between the inlet and outlet) that permits fluid handling, the user gains full control on defining the precise moment in which the liquid will be flown into the microfluidic chamber, fill it in, and push it out of the window area.

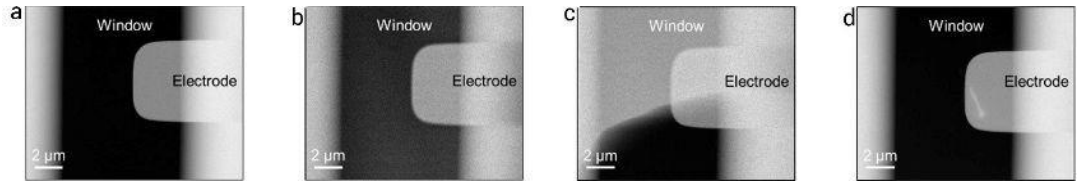


Figure 2. HAADF-STEM images of the window area of a liquid biasing Nano-Cell at different environmental conditions: (a) no liquid, (b) completely filled with liquid, (c) half evacuated and (d) no liquid.

The capability to dynamically change the liquid thickness within the Nano-Cell paves a way to perform in-situ quantitative high resolution and analytical TEM studies, as well as to correlate the experimental results from the micro/nanoscale cell with the ex-situ works that are executed in an unconfined space.

II. Growth and morphology evolution of Cu dendrites

Afterflowingtheelectrolyte, cyclicvoltammetrytechniquewasusedtostudytheelectrodeposition of Cu. To do so, the electrolyte was injected using a flow rate of 1,7 µL/min, and voltage ranging from -0,70 V to 0,30 V was applied to the Pt electrode. Figure 3 shows a time series HAADF-STEM images illustrating the growth and etching process of Cu dendrites. We can directly observe the growth and morphology evolution of Cu dendrites.

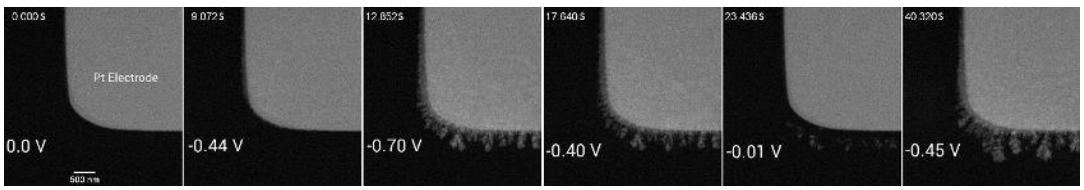


Figure 3. Time series of HAADF-STEM images illustrating the growth and etching process of Cu dendrites on the Pt electrode by employing cyclic voltammetry scanning. In the experiments, incident electron flux was set ~50 e $nm^{-2}s^{-1}$, and the liquid flow rate was 1.7 µL/min.

Thanks to the on-chip microfluidic channel, fresh electrolyte is continuously provided. Moreover, the flow helps to dilute and remove the beam induced species and thus reduce the possible side reactions.

III. Microstructure and chemical composition analysis

Next, SAED analysis was performed. As a dry or thin liquid state is required for electron diffraction, the liquid is pushed out from the microfluidic chamber. Figure 4 a-d shows TEM images of (a) the Pt electrode and (c) the Cu dendrites on the electrode, and (b, d) the corresponding SAED patterns in the liquid phase. The polycrystalline nature of Pt electrode is confirmed by the SAED pattern (Figure 4 a, b). After the electrodeposition, the diffraction rings for polycrystal were resolved. The indication of 220 diffraction means at least a lattice resolution of ~1.28 Å or better can be obtained in the liquid thickness of ~100 nm.

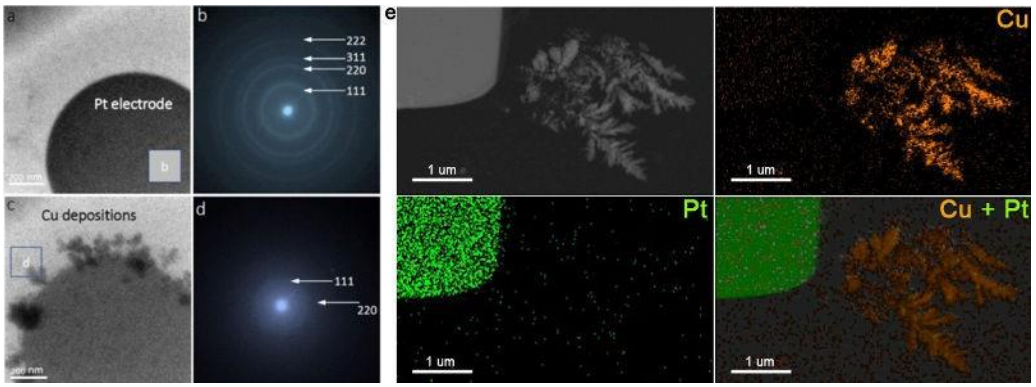


Figure 4. TEM images of (a) the Pt electrode and (c) the Cu dendrites on the electrode, and (b, d) the corresponding SAED patterns in the liquid phase. (e) HAADF-STEM EDX elemental mapping, showing the spatial distribution of the Cu dendrites and the Pt electrode in the electrolyte.

Finally, the chemical composition of the obtained depositions are directly analyzed in the liquid phase. EDX elemental analysis (point, line, or area analysis) is conveniently performed. Figure 4e shows the HAADF-STEM EDX elemental mapping, displaying the spatial distribution of the Cu dendrites and the Pt electrode in the electrolyte, thus confirming the great functioning of this analysis. Thanks to the on chip channel and flow system design, the user is able to push out the (majority of the) liquid, allowing analysis in a dry or thin liquid state, necessary for electron diffraction.

For additional information, contact us by email : contact@fluigent.com or consult our website : www.fluigent.com
DENSsolutions contact: Hugo Perez Garza, PhD - Chief Technology Officer, DENSsolutions
email: e: hugo.perez@DENSsolutions.com - phone +31 (0) 6 53 82 03 19

CONCLUSION

We have demonstrated the use of a complete experimental system consisting in a TEM, advanced sample holder and flow cell, and high precision pressure-based flow controllers for the observation and characterization of copper electrodeposition in liquid phase transmission electron microscopy. The fundamental innovation of this design is the controlled flow. In fact, this design ensures that the liquid is forced to flow between the chips and across the imaging area, as this is the only route for the liquid to reach the outlet. By contrast, other commercially available and in-house fabricated liquid cells have a large volume which relies on diffusion to bring reactants to the viewing area. By directly interfacing the inlet tubing to the microfluidic channel on the chip, the direction and speed of the flow can be precisely controlled. Accordingly, the reactants are driven to the imaging area directly, and the cell can be flushed of reacted species. Finally, this configuration ensures that all the exiting liquid has experienced the same environment and temperature conditions. To the best of our knowledge, no other system either commercially available or custom-built, has employed a dual-chip configuration with on-chip channel.

We kindly thank DENSsolutions for this collaboration, and for sharing the results obtained with their system.

For information about DENSsolutions:
www.denssolutions.com

REFERENCES

1. De Yoreo, J. J. & Sommerdijk, N. A. J. M. Investigating materials formation with liquid-phase and cryogenic TEM. Nat. Rev. Mater. 1, (2016).
2. Hodnik, N., Dehm, G. & Mayrhofer, K. J. J. Importance and Challenges of Electrochemical in Situ Liquid Cell Electron Microscopy for Energy Conversion Research. Acc. Chem. Res. 49, 2015–2022 (2016).
3. Smeets, P. J. M., Cho, K. R., Kempen, R. G. E., Sommerdijk, N. A. J. M. & De Yoreo, J. J. Calcium carbonate nucleation driven by ion binding in a biomimetic matrix revealed by in situ electron microscopy. Nat. Mater. 14, 394–399 (2015).
4. Sugi, H. et al. Dynamic electron microscopy of ATP-induced myosin head movement in living muscle thick filaments. Proc. Natl. Acad. Sci. U. S. A. 94, 4378–4382 (1997).
5. Mirsaidov, U. M., Zheng, H., Casana, Y. & Matsudaira, P. Imaging protein structure in water at 2.7 nm resolution by transmission electron microscopy. Biophys. J. 102, L15–L17 (2012).

6. Peckys, D. B., Korf, U., Wiemann, S. & De Jonge, N. Liquid-phase electron microscopy of molecular drug response in breast cancer cells reveals irresponsive cell subpopulations related to lack of HER2 homodimers. Mol. Biol. Cell 28, 3193–3202 (2017).

7. Ahmad, N., Wang, G., Nelayah, J., Ricolleau, C. & Alloyeau, D. Exploring the Formation of Symmetric Gold Nanostars by Liquid-Cell Transmission Electron Microscopy. Nano Lett. 17, 4194–4201 (2017).

8. Wang, C. M. et al. In situ transmission electron microscopy and spectroscopy studies of interfaces in Li ion batteries: Challenges and opportunities. J. Mater. Res. 25, 1541–1547 (2010).

9. Williamson, M. J., Tromp, R. M., Vereecken, P. M., Hull, R. & Ross, F. M. Dynamic microscopy of nanoscale cluster growth at the solid-liquid interface. Nat. Mater. 2, 532–536 (2003).

10. van Omme, J. T. et al. Liquid phase transmission electron microscopy with flow and temperature control. J. Mater. Chem. C (2020) doi:10.1039/d0tc01103g.