

Liquid Cell Transmission Electron Microscopy for Electrochemical Processes

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Liquid cell electron microscopy enables visualization of liquid phase processes with the high resolution of the transmission electron microscope [1, 2]. Although the technique has been broadly applied for materials and biological imaging, it is particularly well suited for electrochemical studies because its combination of spatial and temporal resolution cannot easily be achieved using other techniques. Observing electrochemical reactions *in situ* requires integration of electrodes within the liquid cell and accurate control of the electrolyte geometry and the electrochemical parameters, voltage or current.

Here we describe the opportunities for liquid cell microscopy to help probe electrochemical processes. We first discuss experimental design. The electrode geometry must be chosen to ensure that the experiment replicates, to as high a degree as possible, the process taking place in a benchtop electrochemical cell. To test this, several types of calibration experiment prove useful. Figure 1 shows two examples for the case of copper deposition [3, 4]. The images shown also illustrate two possible experimental geometries: plan view in (a), where a reaction is imaged on the surface of an electron-transparent electrode, and side view in (b), obtained when growth extends outwards from the edge of the electrode. The experimental geometry can be optimized for the process of interest, whether it is a corrosion reaction, growth front evolution, or additive effects on morphology, these latter two of particular interest for battery operation. It is also important to evaluate electron beam effects on the electrolyte [5, 6] and on the reaction pathway [e.g. 7]. Water radiolysis calculations show complex effects that include changes in pH towards lower values, the creation of bubbles of H₂ or O₂ and the formation of hydrated electrons that react with metal ions in solution to form metal nanocrystals [5, 6].

Additional phenomena can be explored by enhancing the functionality in the liquid cell. Figure 2 shows an example in which liquid flow is used to change the electrolyte chemistry. A galvanic displacement reaction is triggered by adding Pd³⁺ ions to an electrolyte flowing over Ni, forming Pd particles on the electrode. This creates a nanopatterned surface with useful catalytic properties for subsequent electroless deposition. We find a latency time between changes in solution and the visible start of such reactions. Experiments involving a combination of corrosion and beam-induced precipitation [8] can provide information on diffusion processes within the thin liquid cell that may help explain such latency.

The continued development of liquid cell TEM will enable quantitative visualization of an even broader range of processes. Controlled mixing of liquid streams near the viewing area will yield more precise relationships between electrolyte composition and reaction kinetics. The integration of temperature control with electrochemical capabilities will open a new class of reactions for study. Compositional analysis is a new frontier for liquid cell microscopy that we expect will have a strong impact on electrochemical deposition experiments [2]. We therefore anticipate a promising future for liquid cell microscopy for the study of electrochemical processes [9].

References:

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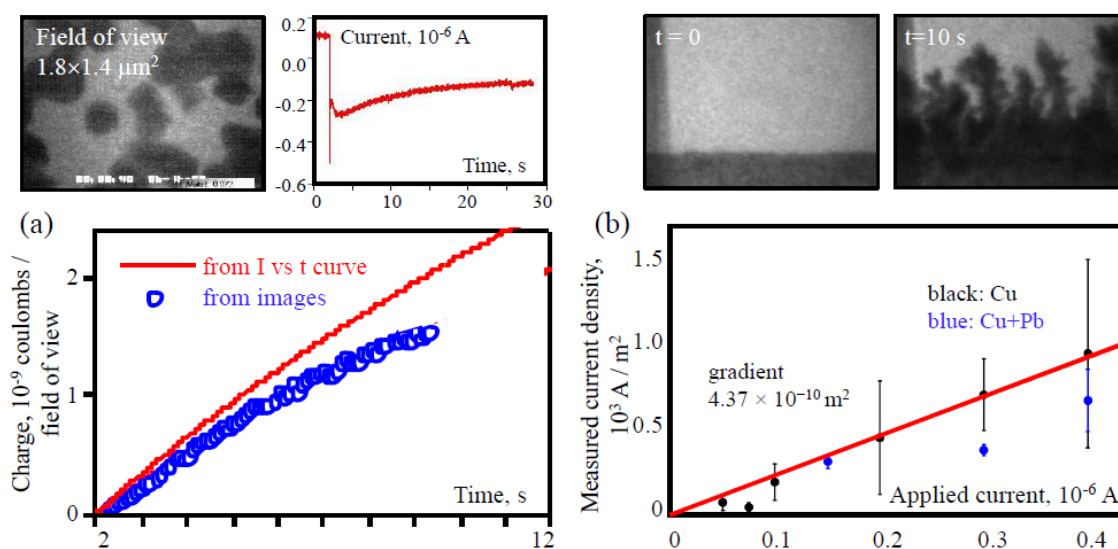


Figure 1. Calibration experiments for liquid cell TEM electrochemistry. (a) Movie frame and current flow for potentiostatic Cu deposition on Au from 0.1M CuSO₄ + 0.18M H₂SO₄ at -0.07V vs. a Cu pseudo-reference electrode. Below, circles show the charge passed through the field of view, estimated from the movie, assuming two electrons per deposited Cu atom and hemispherical Cu clusters (dark features in the image); line shows the charge passed, estimated from the current scaled by the ratio of the imaged area ($2.5 \times 10^{-12} \text{ m}^2$) to the total electrode area ($4.0 \times 10^{-9} \text{ m}^2$). The two estimates agree within 20%, suggesting that the area imaged is representative of the entire electrode area. (b) Galvanostatic Cu deposition on Pt from the same electrolyte with and without Pb additive. Data points show the current density at the imaged area measured from the growth front propagation rate (images above) vs. the total current. The ratio gives the effective area over which current flows. This is similar to the area expected from the geometry of the liquid cell and electrode.

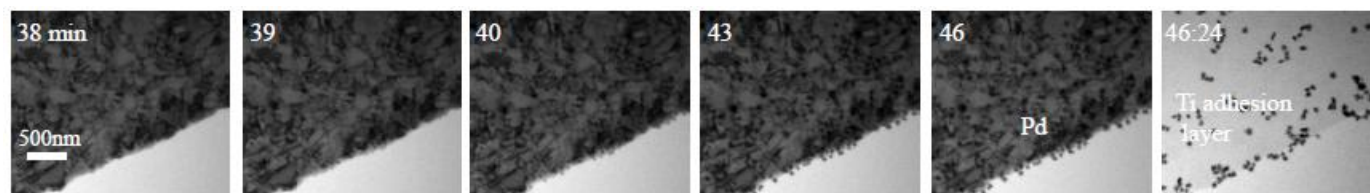


Figure 2. Galvanic displacement of Ni by Pd. 0.1M H₂SO₄ was flowed over Ni then the solution was changed to add PdSO₄. The movie shows that after some latency time Pd particles form on the Ni, consistent with the expected reaction $2\text{Pd}^{3+} + 3\text{Ni}^0 \rightarrow 2\text{Pd}^0 + 3\text{Ni}^{2+}$. Within a few seconds all Ni is removed, partly due to the galvanic reaction and partly a radiolysis effect.