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In situ Liquid S/TEM: Practical Aspects, Challenges, and Opportunities

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Recent advances in the development and implementation of platforms for *in situ/operando* liquid S/TEM experimentation have resulted in new research opportunities in the physical and life sciences, where it is now feasible to routinely image static and dynamic reaction processes of materials in their native liquid environments, at high spatial resolution, and under an external stimuli [1]. (Figure 1) The purpose of this tutorial is to provide a general framework for performing *in situ* liquid cell and electrochemical liquid cell experiments, and to understand the many physical and chemical interactions that can occur during electron beam irradiation. A comprehensive overview of factors such as accelerating voltage, electron dose, cumulative electron dose, and their influence on experimental measurements will be presented.

It has been documented that the highly energetic electron beam, generally used for imaging and spectroscopy, can induce radiolysis within the liquid cell during analysis, which results in the formation of radiolytic species that are both reducing and oxidizing in nature [2]. This principal has been exploited for notable liquid cell nucleation and growth (N&G) studies from liquid phase solutions [3-5]. Calibration of electron dose is crucial such that the amount of radiation damage can be quantified to correlate the electron dose with dynamic observations of N&G processes. Figure 2 shows a typical example from an electron beam-induced N&G study of Pt nanaoparticle growth from a K_2PtCl_6 solution, where annular dark field (ADF) STEM images were acquired at two different electron dose rates. Additional experimental parameters, such as accelerating voltage, TEM vs. STEM imaging, and solution chemistry, have a synergistic influence on experimental results.

The development of electrochemical liquid cells for *in situ* ec-S/TEM has enabled the dynamics of electrochemical processes from electrodeposition [6] to energy storage and conversion systems to be tracked and studied [7-10]. The ec-S/TEM platform incorporates microelectrodes that are directly patterned onto the microchip device such that electrochemical measurements can be performed to either induce an electrochemical reaction or to measure an electrochemical process; e.g., conventional electroanalytical techniques, such as chronoamperometry, cyclic voltommetry, and electrochemical impedance spectroscopy, can be applied during *in situ* ec-S/TEM yielding results that are consistent with the behavior of microelectrodes in microfluidic cells [11]. Figure 3 shows typical *in situ* quantitative electrochemical measurements acquired using an electrochemical microchip with a glassy carbon working electrode, Pt counter electrode, and Pt pseudo reference electrode using a $[Fe(CN)_6]^{3-/4-}$ electrolyte [11]. The primary challenge for performing *in situ* electrochemical measurements continues to be the ability to separate the influence of the electron beam on the electrochemical measurement and selecting the optimal electron dose that is suitable for imaging but does not cause chemical reduction of the electrolyte.

In situ liquid cell microscopy and *in situ* ec-S/TEM have proven to be viable characterization techniques used to investigate nanoscale chemical and electrochemical processes in liquid environments. With future developments in liquid cell microchip design, application of ultrafast imaging and spectroscopy methods, and the utilization of advanced data processing/data mining methods, new scientific breakthroughs are forthcoming [12].

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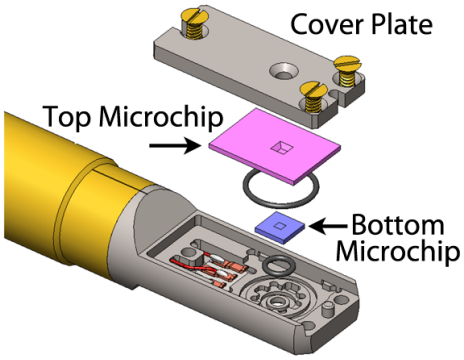

Figure 1. Assembly view of a commercial *in situ* liquid cell and electrochemical liquid cell TEM holder [11].

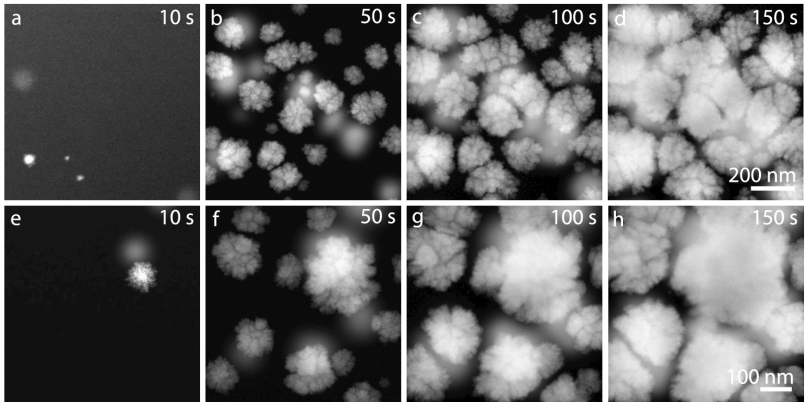

Figure 2. Time-lapse series of ADF STEM images showing the influence of electron dose on the nucleation and growth behavior of nanostructured Pt during electron beam irradiation. (a-d) 50 e^-/nm^2s and (d-g) 415 e^-/nm^2s.

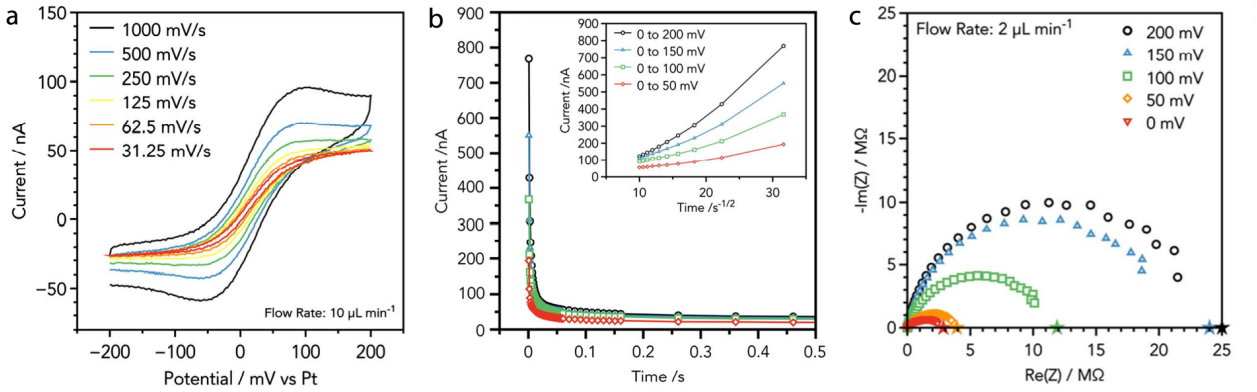

Figure 3. Quantitative electrochemical measurements using electrochemical microchip devices for *in situ* ec-S/TEM and a 2mM potassium ferrocynide/ferricynide electrolyte. a) cyclic voltammetry, b) chronoamperometry, and c) electrochemical impedance spectroscopy [11].

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