Electrochemistry in Liquid Environments

Challenges in the Presence of Accelerated Electrons

Abstract
A meticulous examination of transient stages of dynamic processes at the micrometer, nanometer or atomic scale is the aim in the field of in situ transmission electron microscopy. Studying a specimen in a state close to its native environment without drying possibly leading to structural alterations, triggers research in the field of in situ liquid TEM. However, for any in situ experiment, it is pivotal to accurately consider if the observed dynamic processes are a result of electron–matter interaction or are resulting from the applied stimuli. Therefore, critical aspects for in situ liquid TEM experiments include electron beam stability of the liquid medium, concentration and composition of the liquids in addition to damage free sample preparation on SiN membranes and alignment of the thin observation windows. Efforts towards identifying the critical aspects are discussed. Furthermore, an ergonomic sample preparation setup is pivotal for an easier precise handling of the fragile specimens. An example for such a setup involving micro-manipulators and grippers is shown here.

Introduction
A large number of groups worldwide are working to understand the basic processes that occur at the nanoscale to improve their materials, interfaces, to understand the underlying phenomena or to optimize devices. For this purpose, different characterizing tools are used under in situ and in operando conditions providing key information to understand the aforementioned purposes. The aim is a meticulous examination of transient stages of dynamic processes at the micrometer, nanometer or atomic scale.

In situ transmission electron microscopy (TEM) is at the forefront of such dynamic studies with high spatial resolution [1-4], but still provides significant challenges for research. Applying stimuli such as external fields or forces to TEM specimens turns the TEM specimen chamber into a micro-laboratory in which reactions [5-7], structures [8], or physical properties [9-13] can be initiated, modified or changed at nanometer scale. Ideally, all of these processes are monitored at high spatial and temporal resolutions.
In situ TEM comprises complex sample environments, requiring careful planning of all experimental aspects and the development of precise solutions to correlate with the true operating conditions [14]. For this purpose, different variations of in situ TEM sample holders have been developed, providing thermal (heating, cooling), mechanical (straining, compression), electrical (biasing), atmosphere (liquid, gas, light), ion irradiation, or combinatory stimuli. These facilitate a plethora of in situ TEM capabilities [5] illustrated in figure 1.

In situ TEM has two important components: stimulus and real-time observation. Therefore, a specially designed TEM specimen holder with an optimum specimen and a TEM with a fast image recording system are the important requirements to apply an external stimulus to the specimen and simultaneously perform TEM observations.

One of the major limitations in electron microscopy is that the specimen is exposed to high vacuum leading to the study of completely dried and therefore potentially modified or destroyed specimens. Studying a specimen in its native medium triggered research in the field of liquid TEM [15-20]. This resulted in the necessity of enclosed sample chambers in the TEM. The enclosed chamber should be permeable to electrons and have a low background scattering for good imaging capabilities in addition to optimum mechanical strength to withstand the vacuum, besides being inert to water vapor or other solvents and media.

The first concept for an environmental cell was already developed in 1934 to observe biological specimens in a hydrated state inside the TEM by Marton [21,22]. In 1944, Abrams and McBain constructed the first enclosed wet cell [21]. Difficulties in financial support, instrumentation and resolution resulted in a slow growth of the field. However, recently, liquid TEM has seen a rapid development triggered by the increasing demand in both physical and biological sciences to understand reactions and transitions in materials and complete systems. Thus dynamic in situ electron microscopy is emerging as a tool to meet the challenges of the nanoworld. Correspondingly, sample holder development for liquid and gas phase electrochemistry has increased in the present decade [15] stimulating further research activities.

From the materials perspective, in situ liquid TEM studies were triggered by a variety of research aspects ranging from electrochemical processes in batteries and fuel cells over electrodeposition/stripping, alloying, electrocatalysis to the interaction of biological species with nanomaterials and sensors involving chemical, morphological and structural changes. The wish of any experimentalist would be to
mimic the exact conditions of an *ex situ* system, *in situ* inside the TEM. For example, for electrochemists working on battery systems, observation of interfaces, electrode dissolution / redeposition, solid-electrolyte interphase (SEI) formation, understanding the components of the SEI and their modification during the cycling stages, capacity decay are critically needed to improve battery performance [23].

In this work, we discuss some of the challenges involved in carrying out *in situ* liquid TEM experiments and a setup for ergonomic sample mounting of a liquid system.

**Experimental Setup**

Generally, a liquid cell consists of two silicon MEMS chips with suspended electron-transparent silicon nitride membranes for TEM imaging that sandwich and perfectly seal a thin liquid layer from the TEM vacuum environment (fig.2). To control the electrochemistry *in situ* or *in operando* in the liquid environment, electrical leads are incorporated on one of the devices. Low-noise electrochemical power sources are used to control the electrochemical cycling. The types of materials and electrolytes, the concentrations that can be used within the cell are limited and require extensive planning of the experiments.

The TEM measurements presented here were carried out using an aberration corrected (image) Titan 80-300 (FEI Company). A Poseidon 510 sample holder (Protochips Inc.) was employed for carrying out the *in situ* liquid TEM experiments.

**Challenges**

For carrying out successful *in situ* liquid TEM experiments, it is important to consider and plan the following critical factors: (a) detailed *ex situ* reference experiments, (b) electrochemical environment in the micro-laboratory incl. concentrations and hydrophobicity, possible reactions with the TEM holder components, (c) electron dose and possible imaging modes considering beam-induced modifications and reactions in the electrochemical environment, (d) optimum sample preparation strategies.

**Sample Preparation**

Sample preparation for closed environmental cells involves additional challenges compared to conventional sample preparation [24] to selectively deposit the materials on the TEM windows or the electrodes. Suspended powders can be deposited using microliter tubing. Gas phase deposition has been used to grow thin films directly on the electrodes by selectively masking the device [25], which is challenging because of the small size of the active area [26]. Focused ion beam
preparation and transfer of bulk materials onto the electrodes of the MEMS device is in principle possible \[27, 28\], but care has to be taken to prevent damage of the membranes (hole formation).

The fragile nature of the membrane enclosures is another delicate aspect for sample handling and preparation \[29\]. Both the thickness of the membranes and the liquid layer need to be kept at a minimum for electron transparency \[20\]. However, if the thickness of the membranes is too low, the mechanical handling becomes increasingly difficult. Furthermore, bulging of thin membranes is more pronounced leading to a strong thickness increase away from the edge of the windows, especially if the windows area is large \[15, 20, 29-32\]. Hence optimum dimensions are pivotal to obtain a good signal to noise ratio and limited background intensity. Another important aspect is that any material between the two MEMS devices will increase their distance, thus increasing the liquid layer thickness. Therefore, it is essential to properly clean the devices and work in a dust-free environment. In addition, alignment of both membranes on top of each other within the sample holder is critical to position the edges of the viewing area on top of each other to minimize the liquid thickness. For this purpose, micro-manipulators are useful. Figure 3 shows an example of a micro-manipulator setup, where the sample holder movement is controlled by a X-Y table, fine grippers on an X-Y-Z rotation table can be used to place the fragile MEMS devices on the sample holders together with screws, O-rings and even liquid can be locally applied on the TEM windows through µl-tubing with good precision. Using such a setup makes the alignment of the Si-SiN membranes, their positioning and placement of the liquid using the µl-tubing easier and more ergonomic.

The MEMS devices are sealed by O-ring and also here, it is critical to keep them dust free to prevent leakage into the TEM. To ensure absence of leaks proper leak checks should be carried out at all stages.

Despite the miniaturized size of the \textit{in situ} liquid electrochemical cells, they can be used for a quantitative electrochemical characterization as reported by Unocic \textit{et al.} \[33\], e.g. using cyclic voltammetry, chronoamperometry, or electrochemical impedance spectroscopy. However, for a comparison with bulk electrochemical studies, the thickness of the liquid layer has to be considered as simulations suggest that the conductivity of thin liquid layers is different from that of the corresponding bulk liquid \[34, 35\].

**Interaction of the Electron Beam with the Sample**

The interaction of the electron beam with the sample is critical during \textit{in situ} TEM studies \[21\]. It is pivotal to accurately understand, if the observed dynamic process
is a result of the electron–matter interaction or is resulting from the applied stimulus. To obtain meaningful information during in situ TEM, the effect of electron dose on all the individual components must be understood. This is the key to interpret TEM data, both images and spectroscopic information. However, especially in liquids, radiation damage is subtle and it is difficult to see the primary damage and initial stages of structural changes. Considering liquid electrolytes in batteries as one of the most commonly studied systems, the main components are small organic molecules (carbonates), where similar crystalline materials have been extensively studied and their high beam sensitivity been reported [36]. Recent reports by Gu et al. show the necessity to stay below the damage threshold for beam damage of the liquid electrolytes [28], challenging in situ TEM liquid experiments for in situ batteries at high resolution. Even small modifications of the material and the surrounding environment by the electron beam could alter the following reaction pathway. For example, the interaction of the electron beam with water leads to the formation of free radicals and ions [15, 16, 18, 27, 29, 31, 32, 37, 38] which locally, on a nanometer scale, alters the reaction conditions, e.g. leading to pH variation (fig.2). A partial solution to this is the use of flow cells, where any modified medium is continuously replaced in the active area. In addition, low-dose techniques can be implemented in combination with stroboscopic imaging to reduce the overall dose. Furthermore, beam damage can be tuned by adopting an optimum high tension, to minimize knock-on damage in the bulk or, more critically, of surface atoms or atoms at defects at low voltage or alternatively to minimize ionization damage (radiolysis) at high voltage. However, in complex mixtures of different components, it can be difficult to find an optimum for all of them.

It is well known that the interaction of the electron beam with water creates free radicals and ions in addition to aqueous electrons [33,39]. Also inside the silicon nitride membranes, secondary electrons are generated which are transferred into the fluid to form aqueous electrons [37]. To illustrate these radiolysis effects, we have studied 0.01 M aqueous AgNO3, where the soluble metallic precursor is reduced by the radicals and (solvated) electrons to form metallic silver, which in a second step is aggregating into metal nanoparticles, which can be observed in the TEM (fig.4). By adjusting dose, imaging conditions (TEM vs. STEM), concentration and flow, the kinetics and growth mode of particle formation can be tuned [25]. The difference in growth is qualitatively illustrated in figure 5 for a 0.001M AgNO3 solution imaged with a flow of 5 µl/s. At higher dose, the radiolysis of water even leads to the formation of gas bubbles in the thin liquid film. The bubble can be moved out of the viewing area using a flow-type setup as illustrated in figure 6.

Summary
With the recent developments in the field of in situ liquid TEM, setup and operation
of miniaturized electrochemical reactions in a liquid environment is becoming well established. However, interpretation of the results and correlation with the processes in \textit{ex situ} reference experiments is still a challenge because of difficulties distinguishing electron beam damage, confinement and local depletion effects from the bulk electrochemistry.

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