# Scanning Electron Microscopy to Study the Nucleation and Growth Phenomena in Liquid Electrolytes under Operando Conditions

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# **Abstract Text**

Scanning Electron Microscopy (SEM), while being amongst the most widespread analytical instrumentation, is not widely used to study nucleation and growth (NG) phenomena in liquids. This is, partially due to insufficient exposure of the electrochemical research community to its capabilities. Here, we report on a simple but versatile custom-made setup for liquid phase (LP) SEM to access chemically and electrochemically driven NG processes in liquids. In addition, we will reveal the experimental artifacts and limitations of the technique related to radiation damage of the liquids. Finally, we will discuss a few recent developments in beam damage-free LP SEM imaging in liquids.

## Introduction

The initial but detrimental stages of nucleation and growth e.g., in electrochemistry, usually proceed in a few seconds within the submicron to few micron scales. Standard scanning electron microscopy nicely fits these spatial and temporal domains but cannot be applied directly to processes in liquids or dense gases due to the so-called "pressure gap" between the sample ambient and the high vacuum of the microscope. Attempts to solve this challenge go back to the midst of the last century when thin highly electron transparent membranes were suggested to enable separation of the hydrated samples from the microscope vacuum(1). The progress in implementing semiconductor microfabrication protocols for the needs of the electron and X-ray beams communities during the 1990s resulted in wafer-scale fabrication of a few tens of nanometers thick SiN, SiO<sub>2</sub> (and other materials) membrane chips and their fast implementation as hydrated sample enclosures for standard transition electron microscopy (TEM) (2) and SEM (3) setups (see also corresponding book chapters in (4)).

Here we focus on LP SEM applications given its potential to impact a wider community of NG researchers due to the simple sample holder design, reduced sample size restrictions and facile access to SEM instruments.

There are three major SEM setups used in SEM studies (Figure 1): (i) LP SEM where the liquid sample is contained inside a static or fluidic cell enclosure equipped with 10-100 nm thick SiN membrane window (Fig.1 (a)) and (ii) environmental or variable pressure (E SEM, VP SEM, Fig.1 (b)). The latter relies on deferential pumping of the main chamber with an open sample to maintain acceptable vacuum in the SEM column and cathode. The dynamic vacuum, however, makes it hard to control the solute concentration and its temperature. In addition, many electrolytes are too corrosive to be used inside the SEM chamber.

Finally, a few vendors now offer so-called atmospheric or air-SEM (A SEM) instruments (5-7). In this setup, the entire column of the SEM is capped at the beam exit with a SiN

membrane, thus the electron beam enters the ambient environment and is able to image liquid samples under real world conditions Fig.1 (c).



**Figure 1** a)-c) Three major LP SEM setups. Here, the liquid is designated as dashed dark blue and gas phase as light blue media correspondingly; d)-f) the typical quality of LP SEM images obtained when a high Z-contrast object (Cu or Ag) is: adhered directly to the back side of a 50 nm SiN membrane but yet in liquid (a); separated by ca. 2  $\mu$ m by water vapor (e); the same area as (e) but separated by ca 2  $\mu$ m water layer (f). E<sub>beam</sub> = 30 keV and a back scattered electron detector was used.

The major differences between closed/fluidic cell LP SEM and ASEM are the following. (i) In the LP SEM setup, the object of interest must be in close proximity (<1  $\mu$ m) or adhered to the back side of the SiN membrane to minimize the scattering of incoming and outgoing electrons in order to yield images with ultimate resolution and S/N ratio; (ii) This requirement is relaxed in ASEM due to the much lower density of air enabling the distance between the SiN membrane and the sample to be as large as 100  $\mu$ m. In principle, the air (or vapor) gap can be arranged in LP SEM liquid cell as well. However, it is somewhat a challenge to maintain a precise meniscus position, within 1  $\mu$ m to 100  $\mu$ m, between the sample and the membrane inside the cell. (iii) Finally, there are no sample size restrictions in ASEM while an LP SEM sample is confined by the dimensions of the liquid cell. Figures 1 (d-f) show representative SEM images of the objects (20 nm Ag nanoparticles) immersed in liquid while adhered to the back side of the membrane (d), or a Cu TEM grid separated from the membrane by a few microns of ca 2700 Pa water vapor (e); and the same Cu grid separated from the membrane by a ca 3 mm thick water layer. As can be seen, few nanometers resolution LP SEM imaging is achievable when

the sample is in close proximity to the membrane, however, electron scattering by the membrane, gas, and liquid drastically degrades the resolution and S/N ratio of the SEM as thickness of the liquid layer between the object and the membrane increases.

The emergence of reliable membrane-based liquid phase electron microscopy accelerated NG research; however initial LP SEM studies revealed significant beam effects on NG phenomena in liquids due to high local radiation doses. The beam induced radiolysis chemistry was comprehensively modelled in (8) for TEM setups and revealed that highly focused beams induce local pH change in the solution that can easily alter reaction paths either to nucleation/plating or dissolution/stripping. The later applications of LP SEM therefore split into two main research and development lines: (i) the use of beam effects for material processing in liquids such as lithography (9) or 3D printing (10, 11); or (ii) rationally minimizing these effects to explore true NG phenomena in liquids (12).

While few vendors at present offer closed and fluidic cells for basic SEM imaging of hydrated samples or liquids (3, 13, 14), more sophisticated measurements such as electrochemically, optically, thermally, or chemically induced NG usually require custom designed cells (15-17). One such design is described below in more detail along with its performance to monitor NG phenomena at the nanoscale during electrochemical and chemical processes. In particular electrochemical Ag nucleation, plating and stripping on/from Pt electrodes in AgNO<sub>3</sub> solution and Cu(OH)<sub>2</sub> nanowire growth from Cu upon exposure to KOH and (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution.

#### Experimental

The core of our LP SEM setup is a 5 mm x 5 mm Si/SiN die that contains a KOH etched 200 µm x 200 µm wide 50 nm thick SiN central membrane window (Figure 2a, b). An array of 4 pairs of variably spaced 150 nm thick Pt/Ta finger electrodes and meander microheaters were e-beam evaporated on top of the SiN layer (Figure 2b). Depending on the temperature range and application chemical environment, all electrodes except their 10 µm x 10 µm tips were encapsulated with either 50 nm sputtered Al<sub>2</sub>O<sub>3</sub> or with a spin coated 200 nm thick SU8 resist to insulate from the liquid electrolyte. The Si/SiN membrane chip was vacuum tight glued to the commercial multi-electrode ceramic chip carrier using UV curable epoxy. Note, the use of the standard multi-electrode chip carrier drastically increases the functionality and flexibility of the setup.(17) In fact, both commercial and custom designed SiN (or any other) membrane chips can be used in this setup. The same UV curing procedure was used to isolate all wirebonded parts of the die and chip carrier from the electrolyte (Figure 2c). Two millimeters through-hole was drilled at the center of the multi-electrode ceramic chip carrier to enable electron beam access to the SiN membrane and liquid cell interior. The entire assembly was vacuum sealed with a commercial high pressure liquid chromatography (HPLC) polyetheretherketone (PEEK) flow chamber (T-union) using a silica rubber gasket (Figure 2d). The T-union was machined to host the gasket and to minimize the interior volume of the liquid cell for prompt liquid exchange. The liquid cell was connected to the syringe pump outside the SEM vacuum chamber via 0.38 mm OD PEEK capillary tubing and vacuum feedthroughs (Figure 2e). The syringe pump was operated in suction mode to avoid overpressure inside the cell and membrane rupture. The flow rate through the cell was varied between 0 to  $2x10^{-9}$  m<sup>3</sup>/s, sufficient to replenish the liquid inside the liquid cell within few seconds if needed. The pilot NG experiments below include Ag electroplating from  $10^2 \text{ mol/m}^3 \text{ AgNO}_3/10^2 \text{ mol/m}^3 \text{ HNO}_3$ solution and Cu(OH)<sub>2</sub> nanowire growth upon reaction of  $5x10^2 \text{ mol/m}^3$  KOH and 30 mol/m<sup>3</sup> (NH<sub>4</sub>)2S<sub>2</sub>O<sub>8</sub> solution with Cu (18). In the latter case, Cu was either directly sputtered on to a SiN membrane as a 200 nm thick layer, or holey carbon TEM grid with a 200 nm pre-sputtered Cu layer was gently placed close to the SiN membrane. Due to pressure induced bulging of the SiN membrane under SEM vacuum upon filling the cell with the liquid the distance between the SiN membrane and Cu containing surface was estimated to be between  $10^2$  nm and  $10^3$  nm based on the drop of image resolution. To penetrate and collect measurable electron signal from such a depth, 20 keV to 30 keV primary electron beam and back-scattered electrons (BSE) (and/or so-called type II secondary electrons) were used for image acquisition.



**Figure 2.** a) The structure of the Si/SiN (400  $\mu$ m/50 nm in thickness correspondingly) microchip with a KOH etched 50 nm thick SiN membrane in the center - side view (not to scale). The microchip consists of silicon as the chip base (gray), a 50 nm thick SiN electron transparent membrane (light gray), and Pt/Ta electrodes/heaters (blue/green) encapsulated with an Al<sub>2</sub>O<sub>3</sub> (or SU8) insulating layer. The SiN membrane side with electrodes faces the liquid. b) Design of the microchip - top view. This chip hosts 4 pairs of finger electrodes with different spacing lengths: 10  $\mu$ m, 20  $\mu$ m, 50  $\mu$ m and 100  $\mu$ m. Meander Pt heaters are designated as H 1-2, and H 3-4 electrodes. Guarding electrodes (G) separate the space between heaters and electrodes. c) The microchip carrier (dark gray) with encapsulated wire-bonded parts. d) Gas/liquid fluidic cell assembly; The chip carrier is pressed against the top of a HPLC Tee (light gray) using silicon rubber gasket (red); Two feedthroughs are used for fluidic connections and one as a counter (Ag wire)/reference electrode; e) Electrochemical flow cell (in cross-section) inside the generic SEM chamber.

The design above demonstrates a simple but functional approach to implement LP SEM in any SEM equipped lab using readily available parts. When electrical /electrochemical measurements are not required, the multielectrode chip and chip carrier can be substituted with commercial SiN (Si, SiO<sub>2</sub>, polyimide and etc.) support films for TEM glued to an appropriate size plate with a central hole. The heating option can then be realized using small size commercial Pt cartridge heater (or Pt temperature sensor used as a heater) encapsulated into ceramic or glass housing. When the membrane is made of semiconductor material such as SiC or Si the membrane can be heated by passing the direct current through it. The choice of the ultrathin membrane material depends on particular application and experimental conditions. Some of the LP SEM relevant properties of the commercially available membranes are listed in Table 1.

Window material	Membrane thickness range useful/available for LP SEM	Practical window area for 10 <sup>5</sup> Pa pressure differential (thickness &	Chemical stability	Thermal stability	Other LP SEM relevant properties
		application dependent)			
SiN	5 nm- 100 nm	10 μm <sup>2</sup> -10 <sup>4</sup> μm <sup>2</sup>	Excellent (Dissolves in HF and hot H <sub>3</sub> PO <sub>4</sub> )	Excellent	Non- conducting, optically transparent
SiC	50 nm-100 nm	10 <sup>4</sup> μm <sup>2</sup> -10 <sup>5</sup> μm <sup>2</sup>	Outstanding	Outstanding >1100 K	Conducting, single crystal, high thermal conductivity
SiO <sub>2</sub>	5 nm- 100 nm	10 μm <sup>2</sup> -10 <sup>4</sup> μm <sup>2</sup>	Good (Reacts with strong bases, dissolves in HF)	Excellent	Non- conducting, optically transparent
Si	10 nm- 100 nm	10 μm <sup>2</sup> - 5·10 <sup>3</sup> μm <sup>2</sup>	Good (Reacts with alkaline solutions, HF, HNO <sub>3</sub> )	Excellent	Conducting, can be made single crystal
Polyimide	100 nm -150 nm	$10^4 \mu m^2 - 10^5 \mu m^2$	Excellent (reacts with strong acids and alkaline solutions)	Good (up to 600 K)	Non- conducting, optically transparent

# **Results and discussion**

Electroplating example

To demonstrate the ability of operando LP SEM to probe electrochemical (EC) nucleation and growth processes, one of the finger electrodes was designated as a working electrode and 0.5 Hz scan rate SEM images were videorecorded during cyclic voltammetry (10 mV/s) between the Pt working electrode and Ag counter electrode.



**Figure 3**: LP SEM of Ag plating and stripping reactions at a Pt electrode from a  $10^2 \text{ mol/m}^3 \text{ AgNO}_3/10^2 \text{ mol/m}^3 \text{ HNO}_3$  water solution obtained during cyclic voltammetry. a) Deposition of Ag as the Pt working electrode potential changed from V= 0 V to -0.3 V; Stripping of Ag from V= -0.2 V to 0.5V with respect to the Ag pseudo-reference electrode. The electron beam energy is 15 keV and the scale bar in (a) is 4 µm; b) Cyclic voltammogram of Ag growth and stripping at/from a Pt electrode of two-electrode electrochemical cell; c) d) comparative LP SEM images of the same Ag plated Pt electrode acquired with 5 keV and 30 keV primary electron energy. The panel (d) is reflected along the vertical axis for better comparison with (c); e), f) Corresponding Monte Carlo electron trajectory simulations indicating a drastic increase of the probing depth for 30 keV electrons (f) compared to 5 keV electrons (e).

Figures 3 a, b show voltammogram cycles and corresponding LP SEM images of the working electrode. A nucleation of submicron individual Ag clusters can be observed under a slight overpotential of ca -0.1 V (Figure 3 a). At intermediate potentials (-0.1 V to -0.3 V) both nucleation density and size of the Ag clusters increases. At higher potentials and longer time, a rapid coverage of the Pt electrode with a quasi-continuous Ag film as well as growth of dendritic features can be observed (not shown here). The reverse Ag stripping process occurs when voltage is ramped from ca -0.2 V to 0.5 V. Two sequential cyclic voltammograms of Ag electrodeposition on the Pt electrode (Figure 3b, blue curve corresponds to the first one) show that a characteristic hysteresis appears upon sweeping back from the negative vertex potential followed by a prominent anodic peak due to Ag stripping.

The energy variation of the electron beam can be used to access not only the lateral but also the depth evolution of the deposits. Figure 3 c, d comparatively depicts LP SEM images of the same working electrode during the Ag plating process at 5 keV and 30 keV beam energies. The

observed inhomogeneities in the electrode area are due to Ag clusters that have formed at the bottom of the 200 nm thick Pt electrode. The increased thickness of the newly deposited material leads to higher local electron yield and therefore to the brighter signal. While 5 keV primary electrons are mainly absorbed by the 200 nm thick Pt electrode material and therefore reflect the lateral developments of electroplated material, 30 keV electrons penetrate microns deep into the liquid through the Pt electrode and can provide volumetric information about NG. Corresponding Monte Carlo simulations (19) of the electron trajectories depicted in Figures 3 e and f illustrate this point. Note, that in spite the drastic increase of the penetration depth and the excitation volume for 30 keV electrons compared to 5 keV electrons, the spatial resolution of the LP SEM degrades moderately. The latter is due to the fact, that the majority of the signal forming electrons are formed near the apex of the excitation volume while the rest of the backscattered electrons contribute to the overall featureless background signal. This case-study is a basic demonstration of NG electrochemical capabilities of the LP SEM. More comprehensive EC studies and related LP SEM capabilities can be found in an excellent review (16).

### Chemically induced growth example

In situ LP SEM observation of chemically induced reactions at the liquid/solid interfaces can provide significant insight into oxidation and corrosion mechanisms of metal films and subsequent nucleation and growth of nanoscale architectures involved in semiconductor (20, 21) and catalysis (22-24) research. One such example of this is the chemical etching of Cu with alkaline ammonium persulfate solutions that results in the growth of dense arrays of Cu(OH)<sub>2</sub> nanowires (18, 25, 26). Understanding the NG mechanism of this system has been of significant interest over the past two decades but has remained limited due to lack of high resolution insitu measurements. Ex-situ experiments have suggested that basal growth (18) of the nanowire drives lengthening of the wire structures through oxidation of the Cu surface in the vicinity of the wire structure. This general understanding is reinforced by the observation that wires formed are grown from the existing metal film. Our LP SEM approach can accommodate the necessary environment to observe formation and growth of the Cu(OH)2 NWs in real time as a result of the following reaction:  $Cu(s) + 4KOH(aq) + (NH_4)_2S_2O_8^{2-}(aq) \rightarrow Cu(OH)_2(s) +$  $2K_2SO_4(aq) + 2NH_3(g) + 2H_2O$ . In the first experimental configuration, observation of Cu(OH)<sub>2</sub> nanowire growth was conducted via placement of a holey carbon film, sputter coated with a 200 nm layer of Cu, in close proximity to a 20 nm SiN membrane window. Subsequently, the LP SEM device as demonstrated in Fig. 2d-e was assembled and inserted into the standard SEM chamber. H<sub>2</sub>O was introduced into the fluidic device and an interfacial wetting layer of H<sub>2</sub>O was formed over the course of 20 s after starting the fluidic pump. Then the external H<sub>2</sub>O reservoir was replaced with the etchant solution (see experimental) and a slow (4.10<sup>-2</sup> Hz scan rate) acquisition image (Fig. 4 a) was initiated to capture the temporal evolution of induced Cu(OH)<sub>2</sub> nanowire growth albeit subject to transport dynamics of the etchant solution through the capillary tubing and device. In this configuration, the integrated gray scale value (GSV) along the scanning direction qualitatively tracks the increase in nanowire density during the reaction (Fig. 4b). The GSV increases rapidly initially, but levels-off  $\approx 10$  s after introducing the etchant solution. This result suggests that the overall kinetics, both dissolution of the Cu film and formation of the Cu(OH)<sub>2</sub> nanowire structures, is facile in the presence of the etchant

solution. Plateau of the intensity suggests depletion of the Cu source and lack of dissolution of the Cu(OH)<sub>2</sub> NWs after their formation. A magnified SEM image (Figure 4c) generally reveals sub-100 nm thick wires that are several micrometers long as well as clustering of nanowires, indicating multiple nuclei may initiate in the same vicinity (red arrows in Figure 4c) Furthermore, wires are observed to be extended in varying orientations away from the in-plane film. A visual of the entire window (Figure 4 d) demonstrates that while individual regions have a relatively uniform density of nanowires there does appear to be a general density gradient decreasing from the upper left to the lower right quadrant of the membrane. This observation could be due to a number of factors, two predominate ones being distance of the foil from the membrane and flow patterns of the etchant solution through the device.



**Figure 4**. In-situ SEM measurements of  $Cu(OH)_2$  NW growth from sputtered Cu films. (a) A slow LP SEM scan captures the process of chemical etching that results in the formation of  $Cu(OH)_2$  NW at 200 nm of Cu deposit on a holey carbon film that was gently adhered to 20 nm SiN membrane window. (b) Tracking the gray scale value of a LP SEM scan to monitor the

density of Cu(OH)<sub>2</sub> NW vs. time. (c) Zoomed in in-liquid SEM image of the Cu(OH)<sub>2</sub> NW morphology. (d) Full view of the SiN membrane after Cu(OH)<sub>2</sub> NW growth. (e) In-situ LP SEM images of Cu(OH)<sub>2</sub> NW growth on a 20 nm SiN membrane sputtered with 5 nm Pt and 200 nm of Cu. (f-g) High resolution image before (f) and after (g) formation of Cu(OH)<sub>2</sub> NWs. (h) High vacuum SEM image demonstrating the location of time slice images in (e) and high-resolution images in (i-k). (i) Highlights the sizes, density, and orientation of Cu(OH)<sub>2</sub> NW grown in the 200 nm thick region while (j-k) demonstrate the secondary precipitation of CuO<sub>2-x</sub> platelets from the etchant solution in the Cu deposit free zone.

Further insights into the Cu(OH)<sub>2</sub> nanowire growth mechanism were obtained employing another experimental setup by sputtering a 200 nm layer of Cu directly onto a partially masked SiN membrane. In this experiment a sequential set of SEM time slices are presented at the border region, where approximately half of the area had been masked and thus did not have the 200 nm Cu deposit (Fig. 4 e). Similar growth of Cu(OH)<sub>2</sub> nanowires is observed over the Cu deposit, albeit occurring slightly longer than the experiment using the distanced holey carbon film. Note that complete transformation of the original Cu film (Fig. 4 f) into NWs is observed (Fig. 4 g). Interestingly, new deposits appear in the region where no Cu was sputtered. This deposition qualitatively appears with some delay compared to the growth of the Cu(OH)<sub>2</sub> nanowires which show little difference between the 44 s and 71 s image. Vacuum SEM analysis of the region observed during growth (highlighted in Fig. 4 h-i) depicts the build-up of Cu containing discotic platelets where the Cu film was initially absent (Fig. 4 j). The concentration of these platelets is largest at the border between the two regions (deposit vs no deposit) and decreases away from the film (Fig. 4 k). The average size of the platelets also decreases further away from the original 200 nm Cu film. The observation of deposits away from the original Cu film suggests that dissolution of Cu film may occur more rapidly than redeposition and growth of the Cu(OH)<sub>2</sub> nanowires and thus the concentration of Cu ions in solution can reach a threshold that enables formation of the secondary deposit on the membrane. Interestingly there is a region where neither nanowires nor platelets are observed. Perhaps this gives an indication of the flow field where the concentration of Cu ions is insufficiently high, or the particles haven't reached a critical size to precipitate from solution. Overall, the formation of platelets and their deposition outside of deposited regions suggests that the mechanism of Cu nanowire growth, which densely covered the deposited regions (Fig. 4 h-i) and are hundreds of nanometers to micrometers in length (inset of Fig. 4 i), likely originate from Cu ions in solution that redeposit at nucleation sites on the surface and competes with the basal growth of nanowire structures via migration of surface oxidized Cu. Further exploration of the Cu(OH)<sub>2</sub> nanowire interface with LP SEM could yield additional significant insight into the mechanism behind nucleation and growth. Furthermore, LP SEM could enable understanding of subsequent modification of the nanowires, such as dehydration to produce CuO nanowires or electrochemical reduction to Cu nanowires, which are equally as important in semiconductor, photo/electrochemistry, and catalysis applications.(27, 28)

## The limitations, artifacts in LP SEM and their solutions

As one can see from the above examples, the practical limitation for LP SEM is degraded resolution and S/N ratio as the distance of the object of interest from the SiN membrane increases. While high resolution (compared to *e.g.*, optical microscopy) LP SEM imaging can

only be preserved if the object is located within a few hundred nanometers of the SiN membrane, when liquid is present, the BSE signal, in principle, can be improved if a high electron beam current is used. The latter, however, is limited by the radiation damage of the electrolyte or solvent. Despite a long history of radiolysis studies, the radiation damage of the liquid electrolyte during electron microscopy is an area of active research (8, 29, 30). This is due to the complex spatial and temporal entanglement of excitation/recombination processes, diffusion controlled radiolytic processes and NG processes occurring during LP SEM of the immersed samples. Indeed, even under stationary irradiation conditions, the relative concentrations of the most reactive radicals such as hydrated electrons, OH, H<sup>+</sup>, H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub> etc., strongly depend on irradiation conditions, global and local pH, temperature, and sample morphology. Therefore, common chemistry of EC driven NG processes can be easily affected by these radiolytic phenomena. To exemplify these complexities Figure 5 shows the decay of Ag clusters EC deposited on a Pt electrode by irradiation with 5 keV and 30 keV electrons. SEM beam rastering over a 1  $\mu$ m x 5  $\mu$ m region with 5 keV electrons. A dose rate of ca 10<sup>8</sup> Gy/s leads to dissolution of the Ag deposit into the 0.1 mol/L AgNO<sub>3</sub>/0.1 mol/L HNO<sub>3</sub> water solution within 10 s (Figure 5 (a)). In comparison, irradiation of the nearby area with 30 keV electrons with a similar dose rate does not produce the same effect (Figure 5 (c)). The only difference between these two experiments was the size of the excitation volume (compare Figures 5 (b) and (d)). This indicates that not only the dose rate but also the dose density may play a role in beam induced artifacts.



**Figure 5**. a) The dissolution of EC deposited Ag clusters on Pt upon 5 keV e-beam irradiation with a dose rate of ca  $10^8$  Gy/s; b) Corresponding Monte Carlo simulations of the electron range that roughly corresponds to instant radiolysis reaction volume (dashed line); c) The same as in (a) but excited with 30 keV. No dissolution can be observed when the excitation volume is drastically increased as revealed (dashed line) by Monte Carlo simulations of 30 keV primary electrons trajectories in (d); (e) The LP SEM microscopy realized in transmission mode via electron beam induced X-ray emission

Overall, three approaches can be identified to handle these beam induced artifacts in LP SEM: (i) Theoretical and experimental studies on model systems for better understanding of the radiolytically induced NG processes(16); (ii) Empirical determination of the parametric space for LP SEM where parasitic artifacts can be neglected which requires separate dose test experiments for each system of interest; (iii) Development of new signal acquisition metrologies for LP SEM image acquisition that can operate under reduced irradiation conditions. A good example of the latter approach is the development of electron beam generated X-ray microscopy (31). In this setup, the electron beam does not enter the liquid cell interior but strikes the metal film evaporated onto the SiN membrane acting as point source of X-rays (Figure 5 (e)). These 0.5 keV to 8 keV X-rays have a lower ionization cross-section than the 10 keV to 30 keV primary electrons and therefore induce less radiolitic damage to the liquid. Along these lines there is an interesting recent development of impedance LP SEM (32) where electron beam induced tiny modulations of the impedance of the liquid cell are used for object detection. Though the resolution of these microscopies is still lower compared to standard LP SEM, they offer new contrast mechanisms in addition to being less invasive.

#### Conclusions

The goal of this report is to familiarize the electrochemistry community with basic principles, capabilities, and recent developments in liquid phase SEM microscopy relevant to nanoscopic characterization of nucleation and growth phenomena. The majority of experimental setups still rely on custom-made fluidic enclosures equipped with commercially available few (or few tens of) nanometer thick electron transparent SiN, SiO<sub>2</sub>, Si, SiC or Kapton membranes. The recent progress in fabrication of ultrathin 2D membranes made of one to few layers of graphene, graphene oxide or boron nitride, opens new analytical capabilities for LP SEM (33-37). A spatial resolution of a few nanometers can routinely be achieved by LP SEM under optimal conditions where the sample is adhered to the membrane-liquid interface. Under more general experimental settings, LP SEM still outperforms optical microscopy, provided that the sample is located within 2-3 microns below the liquid surface. Adjustable scanning rate and videorecording allow for imaging of the dynamic processes in the time domain of a few seconds. The major experimental challenge of high-resolution LP SEM studies is beam induced radiolytic phenomena that can affect NG processes at the nanoscale. The latter can at least be partially mitigated by tuning experimental and imaging conditions, or via implementation of less invasive alternative signal acquisition methods. Overall, the implementation of the LP SEM technique for NG studies currently goes in parallel with continuing understanding of the electron beam induced (electro-)chemistry and related phenomena such as spatiotemporal interplay between chemical kinetics and fluidics at microscale (see related discussions in (16, 38, 39)).

### Acknowledgments

Authors are thankful to Dr. E. Strelcov, Dr. Feng Yi, Dr. A. Stevanovic, Dr. J. Velmurugan, Mr. G. Holland and Dr. D.A. LaVan (all at NIST) for their help during different stages of development and tests of the multi-electrode liquid cells.

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