Beam-Sample Interactions During Liquid Cell Electron Microscopy

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Liquid cell electron microscopy is a powerful *in situ* technique that uses the transmission (TEM) or scanning transmission (STEM) electron microscope to image micro- and nanoscale phenomena in liquid media [1,2]. The technique has been used to image phenomena such as nucleation and growth of nanoparticles; electrochemical processes; motion, aggregation, and assembly of suspended nanoparticles; boiling; macromolecular conformations; and biological processes in cells. For better or worse, the electron beam interacts with the sample during imaging and may affect the phenomena under investigation. In fact, many *in situ* crystallization and growth studies rely on the beam to drive the process. The interaction between electrons and the liquid medium, a critically important issue, is only now starting to attract detailed attention from the liquid cell microscopy community. A clear understanding of this issue is essential to account for, suppress, or exploit beam effects.

Although electron beam interactions with solid matter have been studied in detail [3], the situation in liquids differs because of the high mobility of species in the sample. However, the interaction of ionizing radiation with fluid media has been studied by radiation chemists for decades, and is of key importance in nuclear science, medical imaging and therapeutics, food preservation, and other manufacturing processes. Much of the knowledge acquired in these fields is applicable to liquid cell (S)TEM, and conversely, the liquid cell provides a unique tool to study radiation effects. However, it is important to note that the radiation dose-rates in electron microscopy far exceed the levels encountered in most other applications of radiation chemistry.

Here we describe the interactions of high energy electrons with water, finding that radiolysis plays an important role and heating is typically insignificant. In order to develop a model for beam effects, we examine beam-induced bubble formation (Figure 1). We hypothesize that H_2 produced by water radiolysis is the main cause for bubble formation during electron imaging. We then develop a simplified reaction-diffusion model for beam-induced production of H_2 and compare the theoretical predictions with experimental observations of the rate of bubble formation and growth. An example is shown in Figure 2, where the H_2 concentration is calculated in the region around two nearby bubbles. The model predicts that within seconds to minutes of imaging with only moderate beam current, the concentration of H_2 can exceed its saturation concentration, making bubble nucleation possible. Our study yields two key findings. First: radiolysis byproducts formed by the beam quickly reach chemical equilibrium, with a steady-state concentration that is dose-rate dependent. And second: bubble growth is very sensitive and responds superlinearly to beam current.

Based on the results from this study, we suggest that further systematic examination of radiolysis effects specific to the conditions of the electron microscope is of key importance for obtaining quantitative data from liquid cell microscopy. Highly reactive species are continuously produced during (S)TEM observation and the invisible beam effects cannot be dismissed just because there are no bubbles. The byproducts of water radiolysis (primarily: e_h, H_3O^+, H, OH, H_2, and H_2O_2) are strong oxidizing and

reducing agents that are likely to be responsible for a variety of phenomena observed in liquid cell electron microscopy [4].

References:

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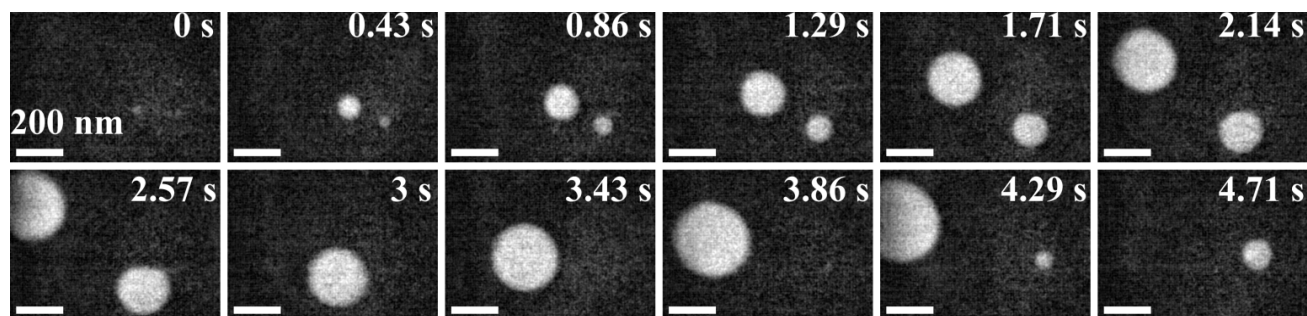
Figure 1: Frames from *in situ* TEM video of bubble nucleation and growth. 300 keV electrons, beam current $I < 1$ nA, and beam radius ~ 2 μm. Two bubbles nucleate on the membrane, grow, and detach. Another bubble nucleates at the same spot and the process repeats.
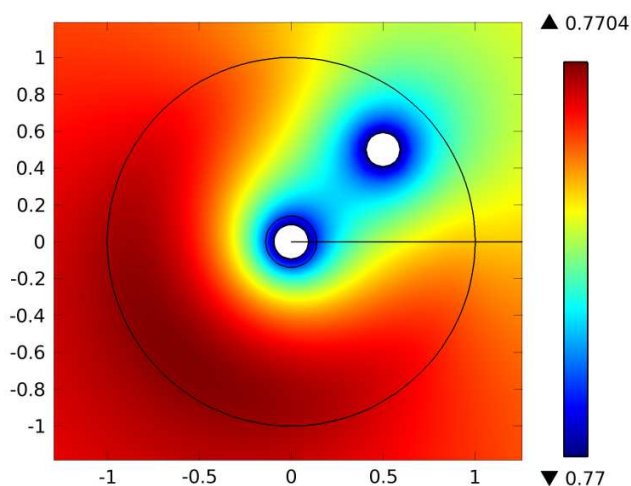
Figure 2: Modeling H_2 concentration in the liquid cell. 300 keV electrons with beam radius of 2 μm (black circle of dimensionless radius 1), and beam current of 0.3 nA. The concentration distribution of H_2 (in mM) is shown when two bubbles (white voids) with radius 185 nm are present. $C_{sat}(100 \text{ kPa}) = 0.77$ mM is specified at the boundaries of the bubbles.