2572
doi:10.1017/S1431927620022072
Microsc. Microanal. 26 (Suppl 2), 2020

Quantifying the Effects of Beam Overlap on Radiation Damage via Radiolysis Products in the *In-situ* Liquid (S)TEM Cell

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In the last decade, *in-situ* liquid cell (scanning) transmission electron microscopy ((S)TEM), has brought new insights and perspectives into various disciplines; for instance, nucleation and growth phenomena, electrochemical reactions, and advances in imaging of biological cells.[1-4] However, despite these significant contributions, liquid-phase electron microscopy (LPEM) has several outstanding challenges. Firstly, the only well-known quantification of radiolysis products is focused on pure water, providing their rate of formation for a given flux of high-energy electrons for a static and parallel TEM illumination only.[5-7] Second, these conditions are very limited and do not consider any alternative imaging modes, such as STEM or Compressive Sensing (CS). In this study, we investigated the various beam conditions for TEM, STEM and CS by employing a reaction-diffusion model and varying the spot size, dose rate, and illumination schemes. As a proof of concept study, we focused on hydrogen gas (H_2) nanobubble formation considering its importance for fundamental aspects of liquid dynamics as well as for preventing undesired damage to the experiments.

It is well known that when an electron beam interacts with a thin liquid layer, radiolysis occurs primarily in the exposed-beam zone. As a result of the localised radiolysis process, the concentrations of the chemical species will not be homogeneous throughout the cell; therefore, diffusion is expected to take place. As illustrated in Figure 1A, a diffusion zone will thus arise around the area exposed-beam zone. Depending on the characterisation scheme being used e.g. TEM or STEM imaging mode,[8, 9] the electron beam can then be moved to another location either by manually changing the sample position or by using a pre-set beam movement scheme (Figure 1B, C). In these cases, if the diffusion of the species from the first beam position is fast/close enough, then they will influence the total concentration of the radiolysis in the second beam position. For this aspect, a particular simulation was carried out for 4 consecutive beam pulses. As shown in Figure 2A, H_2 concentration in the 1st beam pulse overlaps with the radiolytic species generated by the 2nd pulse creating a gradient of radiolytic species spread out across both areas.

Since this overlap occurs as a result of diffusion generated by the species between the pulses, the level of overlap is expected to be dependent on the probe separation distance. In Figure 2B, the H_2 concentration profiles represent the changes as a function of various separation distances between consecutive pulses/beam positions. In a case of 10 nm probe separation, we observe the highest H_2 concentration due to direct overlap of consecutive pulses. Increasing the distance to 100 nm, we observe beam overlap creating an additional shoulder, which increases the diffusion zone and creates a new reaction mixing zone between two consecutive probe areas. As a result, the maximum concentration of H_2 becomes lower as the probe distance increases (Figure 2B). Particularly, in the case of 500 nm probe separation, the high concentration of the reactants in exposed- beam zone do not overlap as the species have time to diffuse away minimising the probability of generating new reactant mixing zone, and therefore, a less chance for H_2 bubble formation.

In summary, we have simulated water radiolysis under various experimental imaging conditions, using a reaction-diffusion model to understand how the distribution of incoming fast electrons affects the overall reaction dynamic and H_2 formation. Using these models, we can predict the distribution of radiolysis products for a range of different illumination and sub-sampling conditions and quantify the threshold condition of the radiation damage, allowing the beam to be used to create well-controlled reactive environments in the in-situ liquid cells. These controls can be applied to any liquid system (not just water) greatly increasing the number of chemical experiments that can be performed in the microscope.

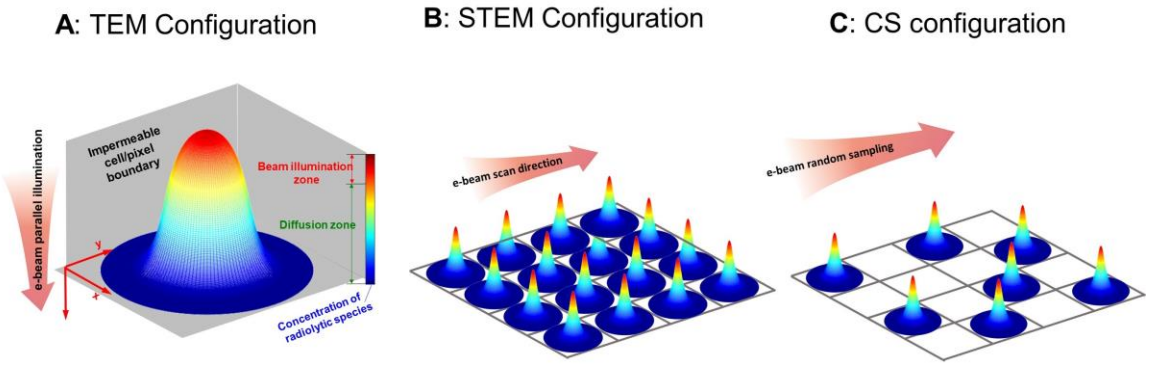

Figure 1. Schematic illustration of the e-beam interaction zones in three different imaging (A) TEM, (B) STEM and (C) random-sampling e.g. compressive sensing mode.

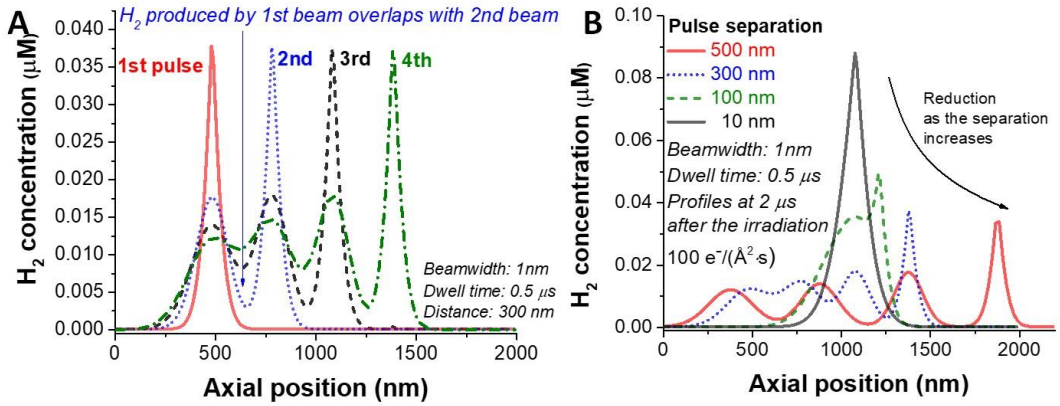

Figure 2. Influence of beam overlap for 1 nm probe size. (A) Spatial concentration profiles of H2 obtained for 4 probe positions with a separation distance of 300 nm and a dwell time of 0.5 µs. (B) probe separation distance in case of 10, 100, 300 and 500nm

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https://doi.org/10.1017/S1431927620022072 Published online by Cambridge University Press

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