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PNNL-30428

Optimizing Sub-Sampled STEM Imaging for Beam Sensitive Materials and Dynamic Processes

September 2020

Nigel D. Browning
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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Summary

The goal of this research is to quantify how sub-sampling and inpainting (broadly classified as methods in Artificial Intelligence) can be used to obtain the highest resolution images under any experimental conditions, and to use this to reproducibly control dynamic in-situ processes in gases and liquids on the nanoscale. As atomic diffusion under non-extreme conditions is typically in the sub-ms time domain, the ability to use this sub-sampling approach to reduce the effect of the electron beam and to speed-up the imaging process represents the optimum combination of spatial and temporal resolution achievable in a conventional microscope. This LDRD funding demonstrated the feasibility of imaging dynamics in complex energy systems using this methodology by establishing the optimum experimental sampling conditions (optimizing the number of pixels, speed, contrast and resolution) for each experiment. For in-situ liquid cell experiments this analysis shows that simply by distributing the same dose and dose rate maximally in space and time, the kinetics for radiolysis products can be modified significantly. The final stage of this work, i.e. the experimental demonstration of its use for nucleation and growth, was severely curtailed by issues with COVID19. However, all the experiments are designed and currently underway, with the goal to complete the final demonstration and publication as soon as safety concerns for laboratory access are met.

Optimum Sub-Sampling Conditions

The motivation for this work is that beam damage to the sample before the highest-resolution images can be obtained is the current limitation in the vast majority of experiments performed in a (scanning) transmission electron microscope (STEM). While the principles behind the fundamental processes of knock-on and radiolysis damage are well-known (as are other contributing effects, such as heat and electric fields), understanding how and when beam damage is distributed across the entire 3-D volume of the sample during an experiment has not been examined in detail. In this project we used standard models for damage and diffusion to elucidate how beam damage spreads across the sample as a function of the microscope conditions to determine an “optimum” sampling approach that always maximises the high-resolution information in any image acquisition. We find that the standard STEM approach of scanning an image sequentially causes damaged regions to be enhanced by diffusion overlaps. These increased damage regions can be significantly reduced by increasing the distance between the acquired pixels in the scan, forming an atomic scale “spotscan” mode of acquisition. The optimum distance between these pixels can be broadly defined by the fundamental properties of each material, allowing experiments to be designed for specific beam sensitive materials. As an added bonus, if we use inpainting to reconstruct the sparse distribution of pixels in the image, we can significantly increase the speed of the STEM process, allowing dynamic phenomena (and the point where damage starts) to be studied directly. Figure 1 shows the benefit of sub-sampling to the effects of beam damage in any experiment. All analyses lie on the same universal plot when they are normalized by probe size, dose, sample thickness and diffusion of damage species. This universal curve means that known parameters can be used for standard experiments and relative changes can be identified for new and complex systems where beam damage mechanisms are unknown.

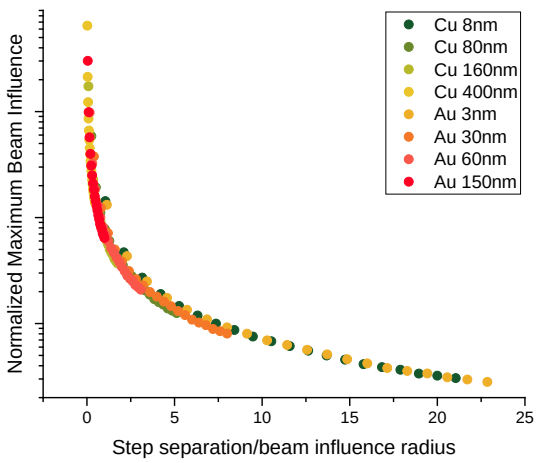

Figure 1: The beam influence (i.e. damage) can be normalized to the mean free path for scattering in a range of different materials. This curve is independent of the intended resolution of the experiment and can be expressed as a function of the normalized probe (pixel) size divided by the probe (pixel) separation. Such curves allow detailed measurements of currently un-quantified damage in complex materials to always be related back to a simple physico-chemical behavior in standard materials.

Designing In-Situ Liquid Cell Experiments

When high-energy electrons from a STEM are incident on a liquid, the vast majority of the chemical reactions that are observed are induced by the radiolysis breakdown of the liquid molecules, i.e. there is beam damage taking place. In the study of liquids, the radiolysis products of pure water are well known, and their rate of formation for a given flux of high-energy electrons has been studied intensively over the last few years for uniform TEM illumination – anecdotally, previous in-situ TEM experiments have seemed to suffer from more beam damage effects than STEM. In this project we demonstrated that the temporal and spatial distribution of the electron illumination can significantly affect the final density of radiolysis products in water and even change the type of reaction taking place. We simulated the complex array of possible spatial/temporal distributions of electrons that are accessible experimentally by controlling the size, the scan rate and the hopping distance of the electron probe in STEM mode and then compare the results to the uniformly illuminated TEM mode of imaging. By distributing the electron dose both spatially and temporally in the STEM through a randomised “spot-scan” mode of imaging, the diffusion overlap of the radiolysis products can be reduced and the resulting reactions can be more readily controlled. This control allows the resolution of the images to be separated from the speed of the induced reaction (which is based on beam current alone) and this facet of the experiment will allow a wide range of chemical reactions to be uniquely tailored and observed in all liquid cell STEM experiments. Figure 2 shows a summary of the results obtained for the production of H2 gas by the radiolysis breakdown of water. Clearly, by sub-sampling the image and moving the beam around, we can greatly reduce the effects of radiolysis on the system as a whole. Similar results have been shown for the other radiolysis products allowing us to tailor the scanning process to a particular desired reaction.

Publications

Distributing Electron Dose to Minimise Electron Beam Damage in STEM, D. Nicholls, J. Lee, H. Amari, A. J. Stevens, B. L. Mehdi, N. D. Browning, submitted *Nanoscale*

Controlling Radiolysis Chemistry on the Nanoscale in Liquids Cell Scanning Transmission Electron Microscopy, J. Lee, D. Nicholls, A. J. Stevens, N. D. Browning, B. L. Mehdi, submitted *ACS Nano*

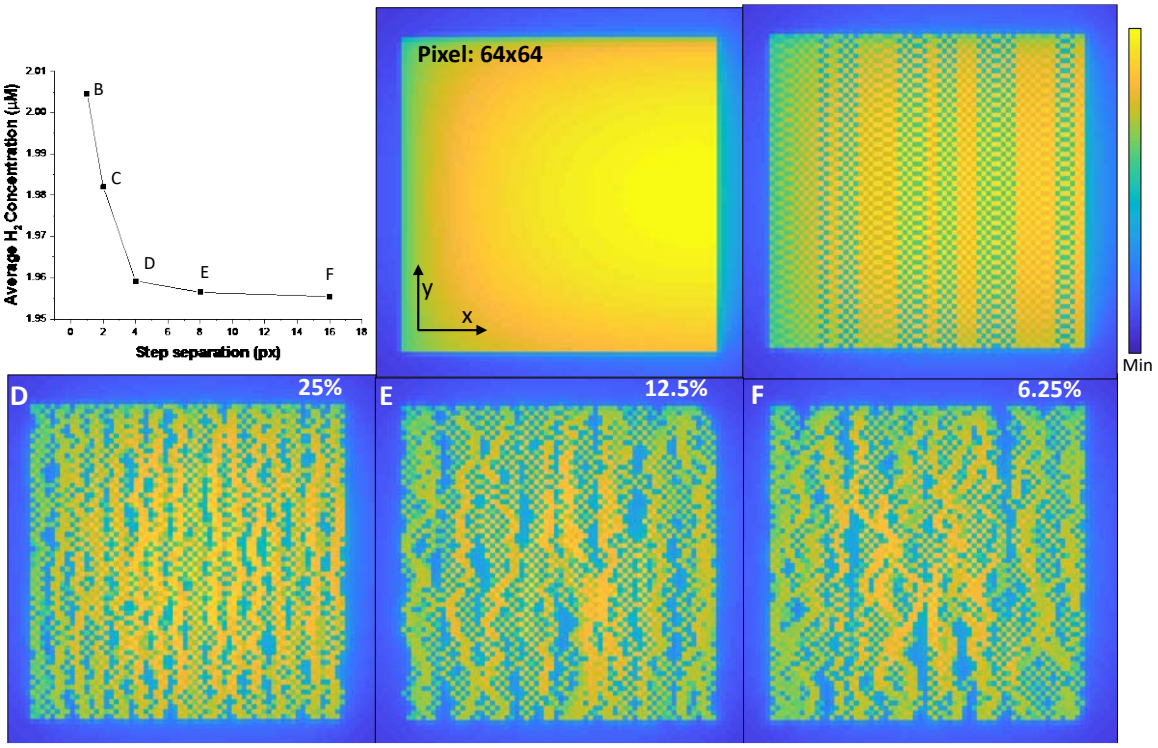

Figure 2: (A) the average H_2 concentration produced from a series of scans obtained with a step separation of 1 pixel (B), 2 pixels (C), 4 pixels (D), 8 pixels (E) and 16 pixels (F). For all scans the total beam dose and dose rate was kept constant with the only difference being the spatio-temporal profile of the beam delivery, i.e. the separation in space and time of the electrons hitting the liquid cell.

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