Panta rhei - tuning the radiation chemistry of silver nitrate solutions via flow in LP-STEM

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Background incl. aims
Operando liquid phase electron microscopy (LP-EM) has revolutionized the insights in chemical reactions. Yet, electron irradiation of liquid phases always comes at the cost of radiolysis. Recent advances in simulation allow to estimate the chemical environment and show that the results are drastically altered for different, diluted aqueous systems[1]. With the new generation of liquid cells however, active flow is feasible experimentally to allow a dynamic exchange of the solution.[2] This demands to systematically access these effects. Recently, flow simulations on irradiation of pure water indicate that the flow reduces the local concentration of some, especially long-lived species. Their lack in turn increases the concentration of short-lived reactive species within the irradiated volume.[3] However, experimental validation is pending - a prerequisite to a mature application of LP-EM to more applied systems.

Recent attention has been drawn to silver nanoparticles for CO2 upconversion. To facilitate such studies in in LP-EM, the radiation chemistry of such systems must be well understood. While the radiation chemistry of AgNO3 was estimated in TEM, STEM, and under heatin[4], the impact of direct flow on beam-induced Ag nanoparticle evolution remains an unknown parameter.

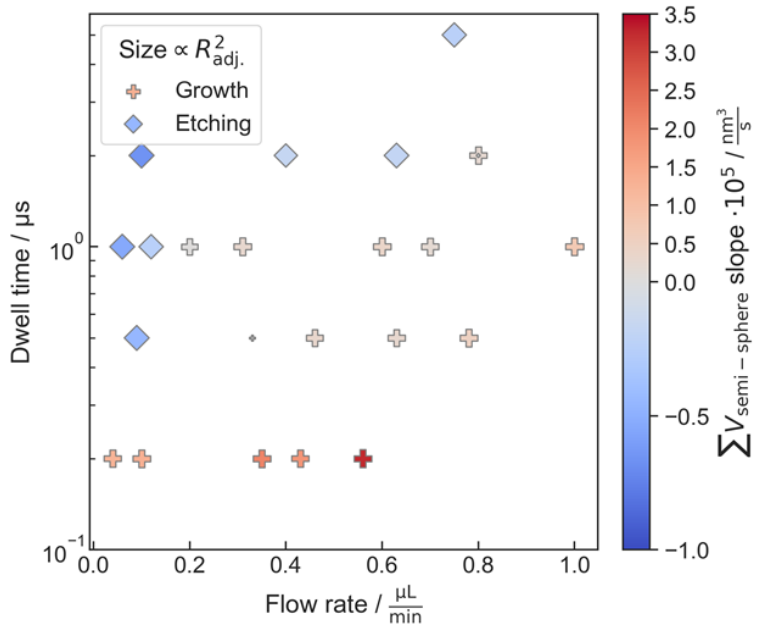
Methods
To overcome this knowledge gap, we provide systematic experiments using a DENSsolutions Stream system and a Thermo Fisher Scientific Talos F200i at 200 kV in STEM mode operated with a beam current of 22 pA. By using AgNO3 as probe solution, we systematically vary flow velocity and dwell time to characterize growth and etching kinetics.

Results
Our findings show that radiolytically-grown Ag nanoparticle behavior ranges from fast growth to dissolution, suggesting a change between reductive and oxidative regime. This is achieved by a change of either flow rate or dwell time, which allowed to empirically map the parameter space. Preliminary results are shown in Figure 1: Growth rate analysis of silver particles

(colorbar) for varying dwell times of the scanning electron beam (y-axis) and flow rates(x-axis).

Supporting to the experimental analysis we provide further advances to the automated radiation chemistry tool AuRaCh[5] including interrupted (scanning) irradiation and flow. These findings will provide further insight into the chemistry observed in flowed liquid-phase experiments.

Graphic:



Keywords:

LP-EM, silver nanoparticles, flow velocity

Reference:

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