Quantification and Control of Mass Transport in different Liquid-Phase Transmission Electron Microscopy Flow Scenarios

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Background

Liquid-phase transmission electron microscopy (LP-TEM) is an emerging experimental technique which permits the monitoring of processes in liquid samples with nanometer-scale resolution. Over recent years, LP-TEM setups have evolved into sophisticated model reactors for the study of physico-, bio- & electro-chemical processes propelled by the integration of various stimuli such as temperature, electric bias, and reaction media composition. In particular, microfluidic systems have inspired numerous expectations among the community, most notably the control of supply of reagents to and/or reliable removal of unwanted (radiolytic) species from the imaging region. However, the evolution of LP-TEM into a quantitative imaging technique remains limited by several issues, most of which are related to poor calibration of mass transport dynamics in the complex LP-TEM flow channel geometries.[1] Here, we will discuss fundamental aspects of mass transport in LP-TEM flow experiments.

Methods

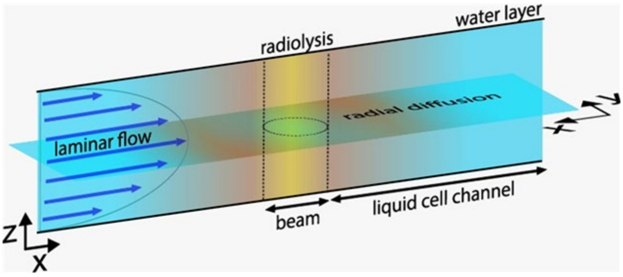
A general approach combining experimental and theoretic methods for the calibration of mass transport in LP-TEM flow systems will be described.[2] The experimental part relies on image contrast variation achieved by flowing a contrast agent. The theoretic part relies on finite element modelling of relevant physics, i.e. convective and diffusive transport, in realistic 3D channel geometries. Both aspects will further be implemented in a rapid prototyping procedure for the fabrication of novel LP-TEM flow reactors: a virtual prototyping step that relies on an experimentally validated model is combined with a physical prototyping step that uses microfabrication routines (lithography and wet-etching). In addition, to study the impact of the established mass transport mechanisms on beam-induced chemistry, the finite element model is further extended by reaction kinetics of radiolysis.

Results & Discussion

A comprehensive understanding of mass transport phenomena in LP-TEM flow scenarios will be provided. First, the bimodal approach is applied to understand the hydrodynamic properties of different LP-TEM flow reactor geometries. In particular, crucial geometric features of the flow channels are identified that result in either convection or diffusion being the dominant transport mechanism.[2] Second, the effect of convective transport on radiolytic reaction networks will be investigated.[3] In contrast to established assumptions, only molecular radiolytic species can be rinsed effectively. In consequence, the concentration of highly reactive species (e.g. H* and e-) follow non-linear trends and increase with increasing flow velocity. The implications of these findings for flow-based scavenging strategies will be highlighted. Thereupon, novel LP-TEM flow setups with diffusion-optimized mass transport properties, which exceed previous constraints by ~2 orders of magnitude, will be presented.[4] Finally, the benefits of the novel setups are demonstrated through different application examples from the field of materials reasearch and electrochemistry.[5]

We anticipate that the knowledge provided will enable better planning of in situ & in-operando experiments and support more reliable interpretation of results. The rational design of flow reactors will enhance correlatability to ex situ experiments and open new fields of LP-TEM research.

Graphic:



Keywords:

Liquid-Phase TEM, microfluidics, in-situ experiments

Reference:

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