

In-situ Electrokinetics Using Liquid Phase Transmission Electron Microscopy

Mads S. Larsen¹, Murat N. Yesibolati¹ and Kristian S. Mølhave¹

¹ DTU Nanolab, National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Lyngby, Denmark.

The ability to observe in-situ nanoscale events using liquid phase transmission electron microscopy (LPTEM) [1] has facilitated a wealth of new insights into chemical processes, including the nucleation of nanoparticles [2-3], dendrite growth [4] and lithiation/delithiation studies [5].

However, one key challenge in LPTEM is accounting for the effects of electrostatic forces in liquids at the nanoscale, as the systems and processes observed are on the nanoscale and often within the Debye layer thickness [8]. The typical commercial LPTEM system is based on silicon nitride membranes (see **Figure 1(a)**), where surface charges are unavoidable due to the interaction between silanol and silylamine sites with water molecules [6]. Additionally, charging of the silicon nitride occurs while imaging with the electron beam and the consequential radiolytic effects further complicate the reactive environment through altered chemical composition [7]. These charges can also have an effect on the flow inside nanoscale confined liquid through electrokinetic effects [9].

We here quantify electrokinetic phenomena in order to understand their role in the observation of slow or non-brownian motion of attached and freely moving particles with LPTEM [9-11]. Electrokinetic effects such as electroosmosis (EO) and electrophoresis (EP) may also lead to new features for system control in LPTEM and aid in understanding beam induced effects.

Using a custom built LPTEM system with two clamped chips with silicon nitride membranes and 50 nm Au/ 5 nm Ti electrodes (**Figure 1(a)**), we are able to produce controlled electroosmotic flow, from which it becomes possible to deduce the zeta potential of the SiN_x film. The sample was a 0.1mM Na₂SO₄ electrolyte. To produce the EO flow, an *Ivium Compactstat.h* was set to produce a DC square pulse at different voltages and polarity, with connections as shown in **Figure 1(a)** and **Figure 1(b)**, where the working electrode (WE) and sensing electrode (S) jointly biasing relative to connected counter electrode (CE) and reference electrode (RE). The 3 center electrodes were all connected to the WE to avoid any floating electrodes. The experiment was first performed in an Olympus B51X optical microscope recorded with a UI-1465-LE-C-HQ camera at 20fps, and then in a TFS Tecnai T20 TEM at 200kV in TEM mode recorded with a TVIPS XF416 CMOS camera at 5fps. The screen current was recorded on the phosphorous screen of the TEM and was fixed to 0.826nA (0.03e⁻/Å²s). Data was later analyzed using ImageJ in combination with Python.

When performing the experiment in the optical microscope, different colors are reflected depending on the liquid layer thickness. To assess liquid thickness, the reflected light color was simulated in Python, see **Figure 2(a)** for a SiN_x-Water-SiN_x multilayered structure. From the color we deduce the liquid thickness, see **Figure 2(b)** for an example DC experiment at ±0.5V. The TEM results are analyzed by subtracting the average image of a 0V reference video from the video, results are shown in **Figure 2(c)**.

Our findings show that as the voltage is increased with respect to the CE/RE, the liquid thickness increases, while a negative voltage leads to a decrease in thickness. This implies that the surplus of ions

in the double layer are positively charged, meaning the zeta potential of the SiN_x membrane is negative. The increase in EO pressure agrees with our analytical model developed as part of this study, currently under refinement to make quantitative measurements and comparisons with varying beam dose rates to assess beam influence of membrane charge state.

These preliminary results show how a thin, flexible, SiN_x film can be used to measure local electroosmotic pressure, which in turn can reveal information about local surface charges and the corresponding zeta potential. The EO results can be further used when investigating EP flow of nanoparticles to subtract the contribution from EO flow. In this way essential quantitative knowledge can be obtained for the surface charge state of samples in LPTEM [12].

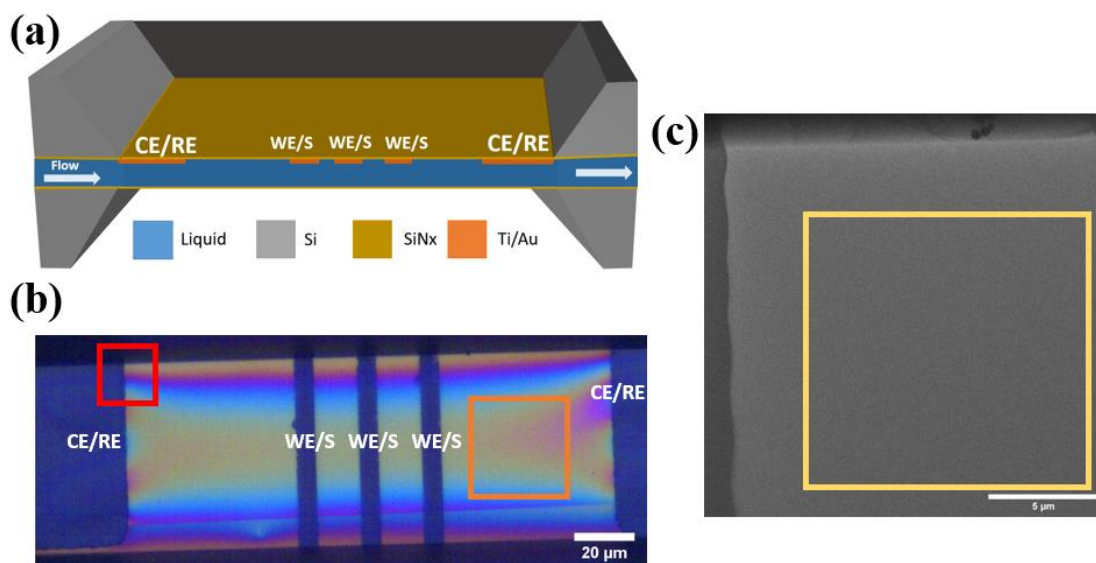


Figure 1: (a) Schematic of the LPTEM cell, (b) optical image of the top chip of the clamped system, abbreviations of the electrodes can be found in the text, and (c) showing the BF TEM, the yellow box indicate where the image analysis was done, the scale bar is 5 μm. Boxes colors: Red; where TEM was done, orange; where optical microscopy analysis was done, and yellow; where TEM analysis was done.

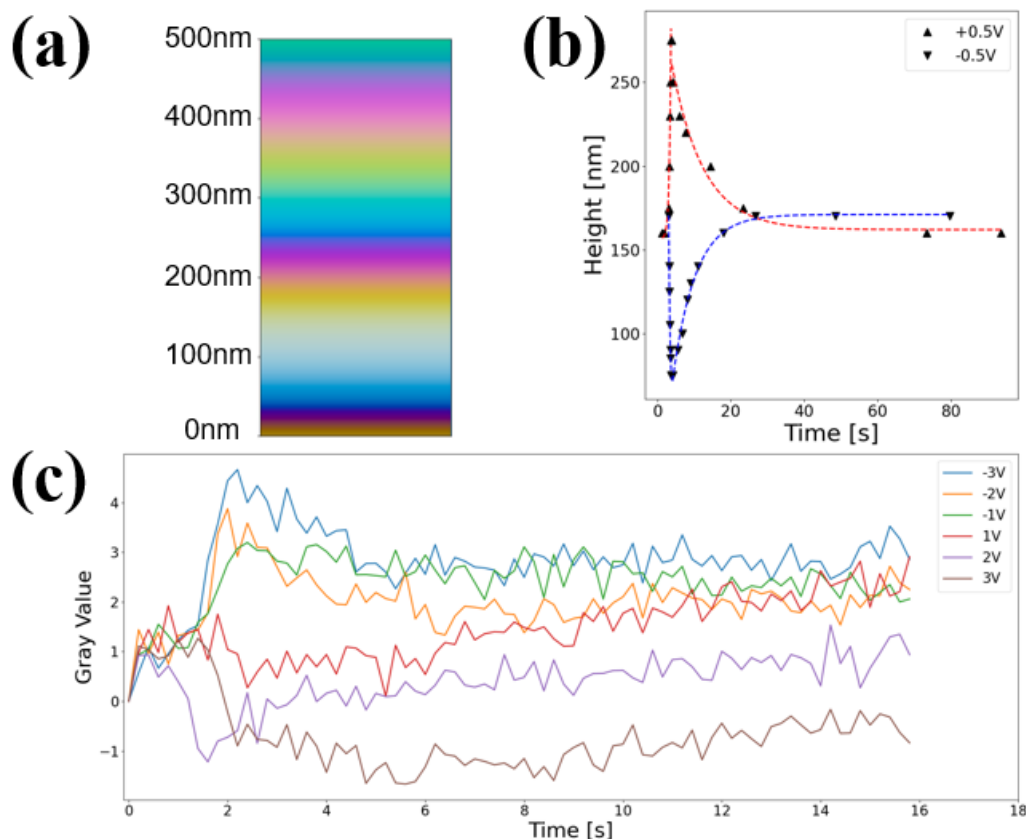


Figure 2: The color spectrum obtained from a SiN_x-Water-SiN_x multilayered structure, and experimental results from; (b) the experiment in an optical microscope at $\pm 0.5V$ (orange box, **Figure 1(b)**), and (c) the experiment in the TEM at different DC voltages (yellow box, **Figure 1(c)**).

References:

- [1] F Ross in “Liquid Cell Electron Microscopy (Advances in Microscopy and Microanalysis)”, ed F Ross, (Cambridge University Press, Cambridge), p. 3.
- [2] N Ahmad et al., *Nano Letters* **17** (2017), p. 4194..
- [3] B Song et al., *Nanoscale* **10** (2018), p. 15809.
- [4] Y Wu and N Liu, *Chem* **4** (2018), p. 438.
- [5] M Gu et al., *Nano Letters* **13** (2013), p. 6106.
- [6] SG Malghan, *Colloids and Surfaces* **62** (1992), p. 87.
- [7] NM Schneider et al., *Phys. Chem. C* **118** (2014), p. 22373.
- [8] Y Green, *J. Chem. Phys.* **154** (2021), p. 084705.
- [9] MN Yesibolati et al., *Nano Lett.* **20** (2020), p. 7108.
- [10] TAJ Welling et al., *Part. Part. Syst. Charact.* **37** (2020), p. 2000003.
- [11] A Verch, M Pfaff and N de Jonge, *Langmuir* **31** (2015), p. 6956.
- [12] We acknowledge financial support from DTU Nanolab at the Technical University of Denmark, Danish Research Council for Technology and Production Case No. 12-126194, and in part by the Advanced Materials for Energy-Water Systems (AMEWS) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.