Liquid Cell TEM

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20-11-18

Why?

- Transmission electron microscopy offers structural and compositional information with atomic resolution, but its use is restricted to thin, solid samples.
- Liquid samples, particularly those involving water, have been challenging because of the need to form a thin liquid layer that is stable within the microscope vacuum.
- Liquid cell electron microscopy allows us to apply the electron microscope to imaging and analysis of liquid specimens.

Gradual Developement

1. **Open cell approach : Use of differential pumping to enable a high enough pressure at the sample region to allow water droplets to condense.**
   - ❑ Success : in TEM for electrochemistry involving low vapor pressure ionic liquids, to understand materials transformations during Li-ion battery operation.
   - ❑ Disadvantage : the droplet geometry was not controlled and the maximum pressure was limited.

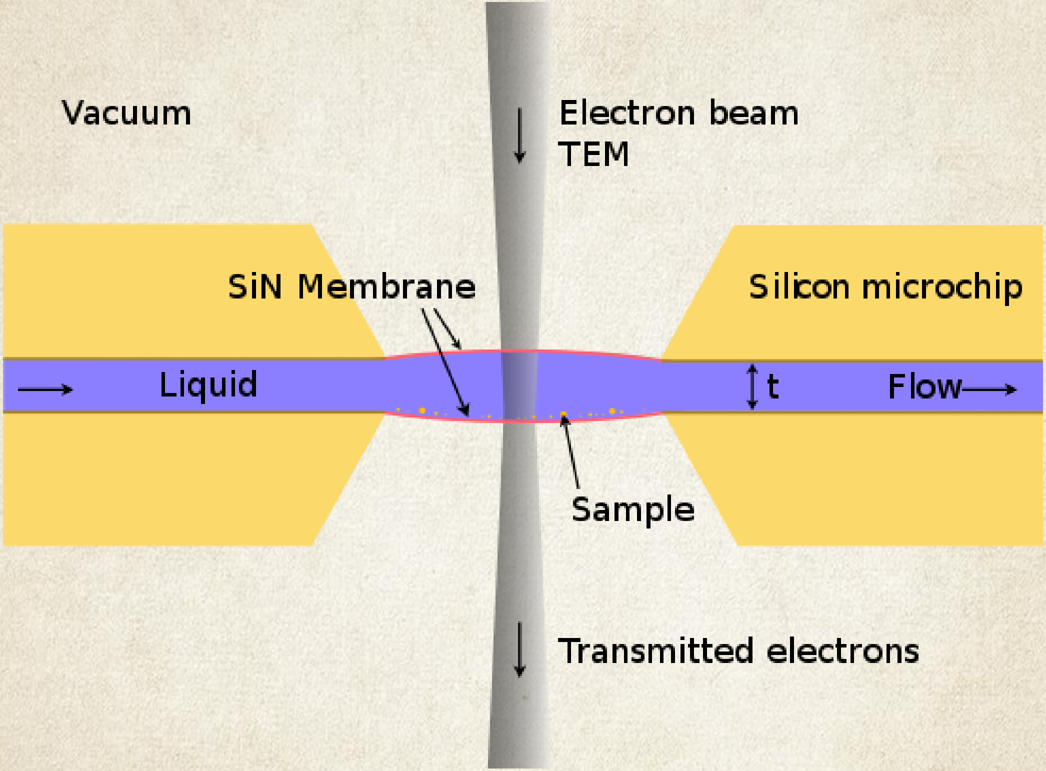
2. **Closed-cell electron microscopy : Enclosing water between two electron transparent windows circumvented the limited maximum pressure of the open cell.**
   - ❑ Disadvantage : the resolution was reduced by the thick windows used (nitrocellulose, collodion) and it was difficult to control the window separation.

Gradual Developement

3. Advanced closed-cell approach : Closed liquid cells made by modern microfabrication techniques using thin silicon nitride windows.

Initial liquid cells were homemade, somewhat unreliable, and sealed the liquid hermetically with glue.These are now simpler to use and available commercially.

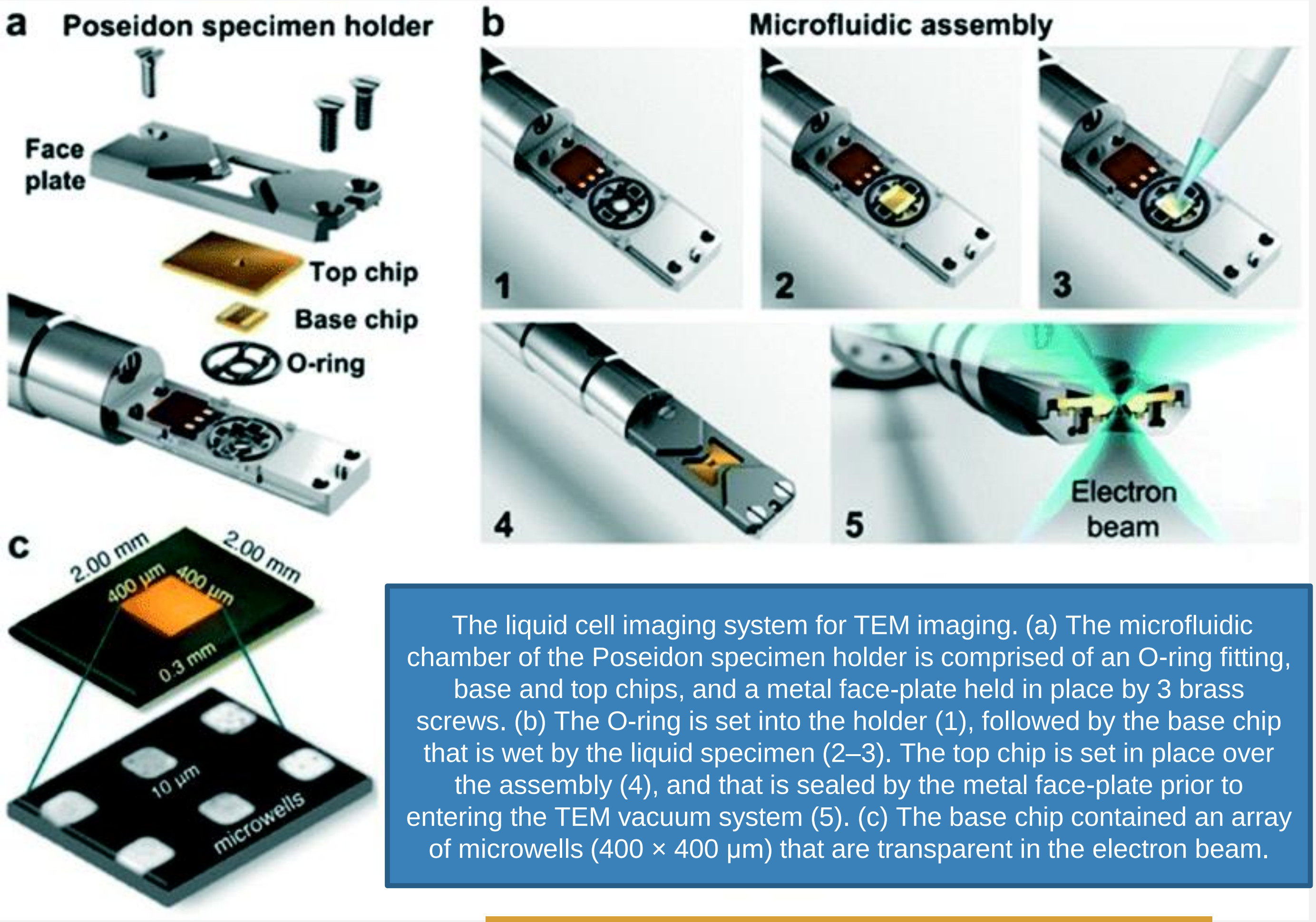
Schematic & Principle



The liquid specimen: enclosed by two membrane windows supported by silicon microchips. Thickness of the liquid, t : sufficiently small w.r.t. the mean free path length of electron scattering in the materials, so that the electron beam is transmitted through the sample for detection.

Components : The cell

- Criteria :
  - Electron transparent yet can withstand the 1-atm pressure difference between the cell interior and the microscope vacuum.
- Material used
  - silicon nitride
- Method of preparation :
  - Thin film of SiNx deposited onto a Si wafer.
  - the silicon is etched from the back to form 100 µm thick windows.
  - The wafer is diced into chips, each containing a window.
  - Two such chips are placed face to face, with a spacer material between. This confines the liquid within a thin layer.



The liquid cell imaging system for TEM imaging. (a) The microfluidic chamber of the Poseidon specimen holder is comprised of an O-ring fitting, base and top chips, and a metal face-plate held in place by 3 brass screws. (b) The O-ring is set into the holder (1), followed by the base chip that is wet by the liquid specimen (2–3). The top chip is set in place over the assembly (4), and that is sealed by the metal face-plate prior to entering the TEM vacuum system (5). (c) The base chip contained an array of microwells (400 × 400 µm) that are transparent in the electron beam.

DiMemmo et al, *Lab Chip*, 2017, **17**, 315-322

Components : Others

- To complete the liquid cell, the chips may be glued, wafer-bonded, or squeezed by clamping in the holder using small o-rings.
- The spacer may be a solid layer with a channel, or spherical particles.
- The liquid may be inserted through an entry port etched into one chip or flowed in through the gap between the chips.
- Electrodes can be patterned lithographically inside the closed cell and controlled by an external potentiostat.
- A heating element or cooling capability can be integrated, and the silicon nitride surfaces can be patterned or chemically modified to enable reactions with species in solution.
- The sample holder carries the electrical connections between electrode or heater elements and their external controllers.

Disadvantages: Low image resolution

- Resolution is lost through multiple scattering of the electrons in both the liquid layer and the window material.
- The liquid layer is usually thicker than desired, especially toward the center of the window, because the windows bulge outward due to the pressure difference.

Disadvantage : Electron beam effect

At the energies used in electron microscopy, the beam causes radiolysis of liquids, including water. Among these radiolysis products,

- Hydrogen gas can exceed its solubility limit and form bubbles, which alter the liquid geometry.
- Hydrogen ions can change the solution pH.
- Highly reactive electrons cause beam-induced growth of metallic nanoparticles by reducing metallic cations.

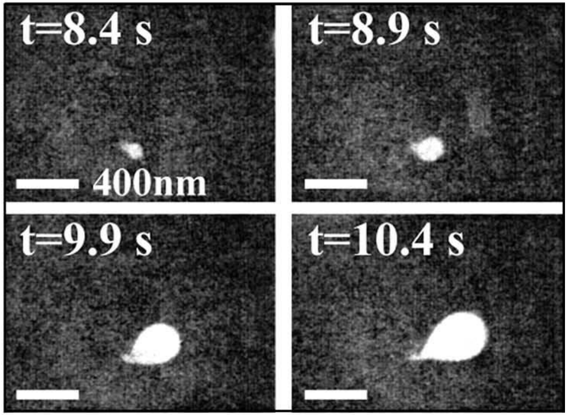
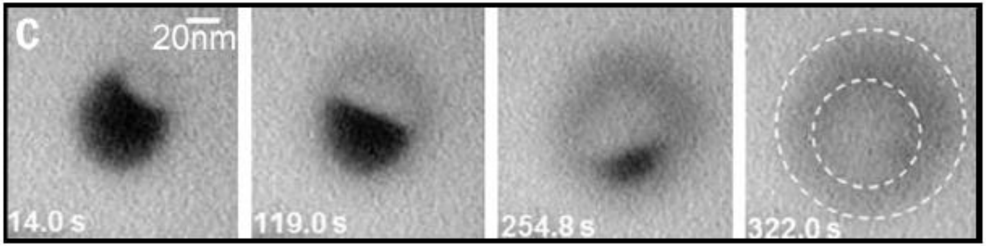
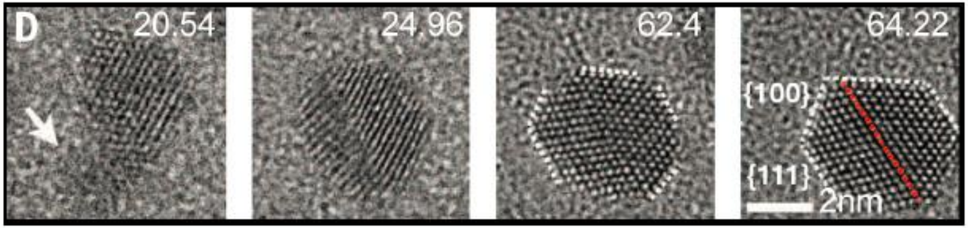


Image series showing heterogeneous nucleation, growth, detachment, and migration of radiolytic hydrogen bubbles formed during TEM imaging at 300 keV, beam current < 1 nA and beam radius ~2 mm.

Applications



The formation of a hollow void in an oxidized Bi nanoparticle via the Kirkendall effect, dominated by nonuniform diffusion of bismuth.



Sintering of two particles (smaller one arrowed), conversion of the grain boundary into a planar twin boundary, and evolution toward a hexagonal shape.

Thanks!

Any questions?

Ref:
Opportunities and challenges in liquid cell electron microscopy
Frances M. Ross
Science, 18 DECEMBER 2015 • VOL 350 ISSUE 6267