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Controlling Temperature in the CINT *In-Situ* TEM Liquid Cell

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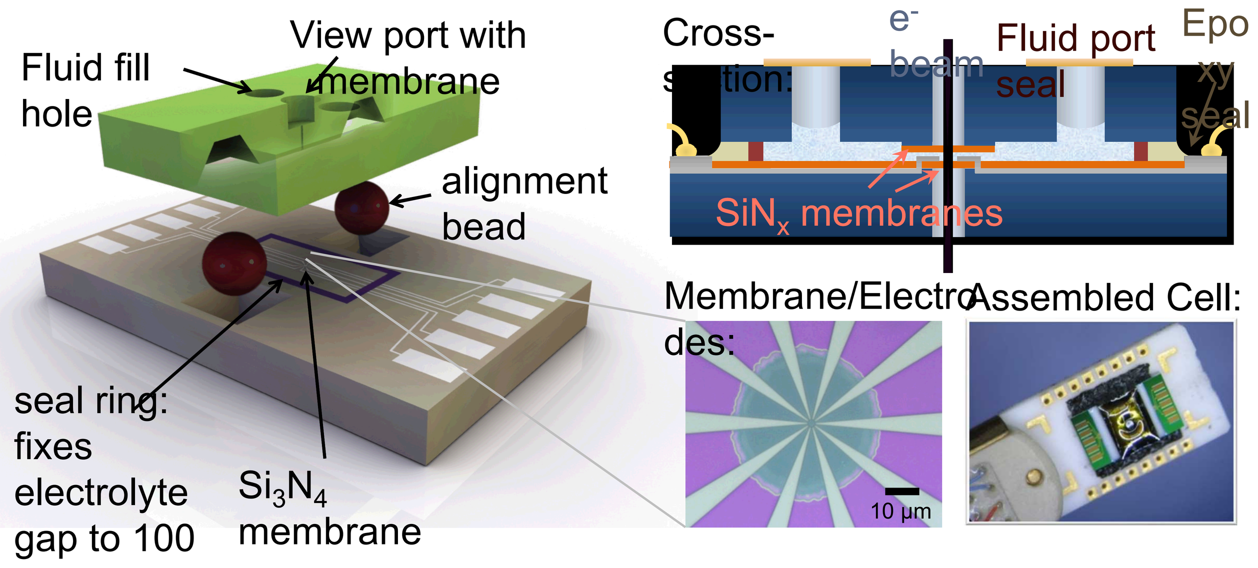
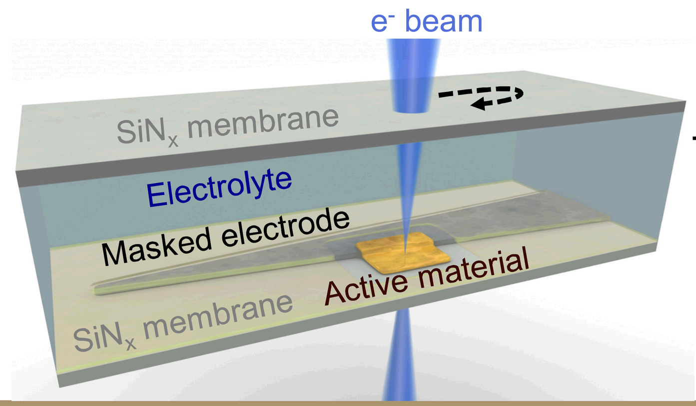
Background: Microfabricated TEM liquid cell

High-resolution TEM imaging of materials in **volatile liquids** enabled by a custom microfabricated, sealed cell with electron-transparent membranes.



Materials of study in liquid or on electrodes; cell filled with ~100-nm thick liquid layer.



Active material can be fully visible in TEM field of view.

Controlled rate links images with

Goal: Add heating to control kinetics.

Applications:

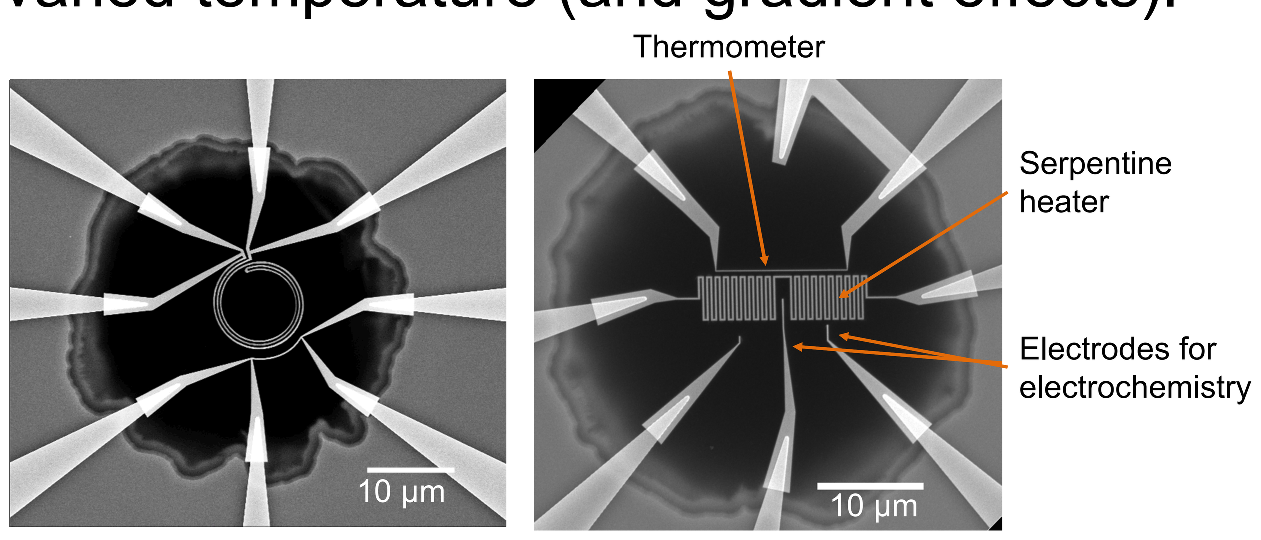
- Nanowire growth
- Thermal batteries
- Additives in electrodeposition
- Self assembly of nanoparticles
- Solute precipitation/dissolution
- Protein denaturing

$$D_{solid} = D_0 e^{-Q/k_b T}$$

$$D_{liquid} = \mu k_b T$$

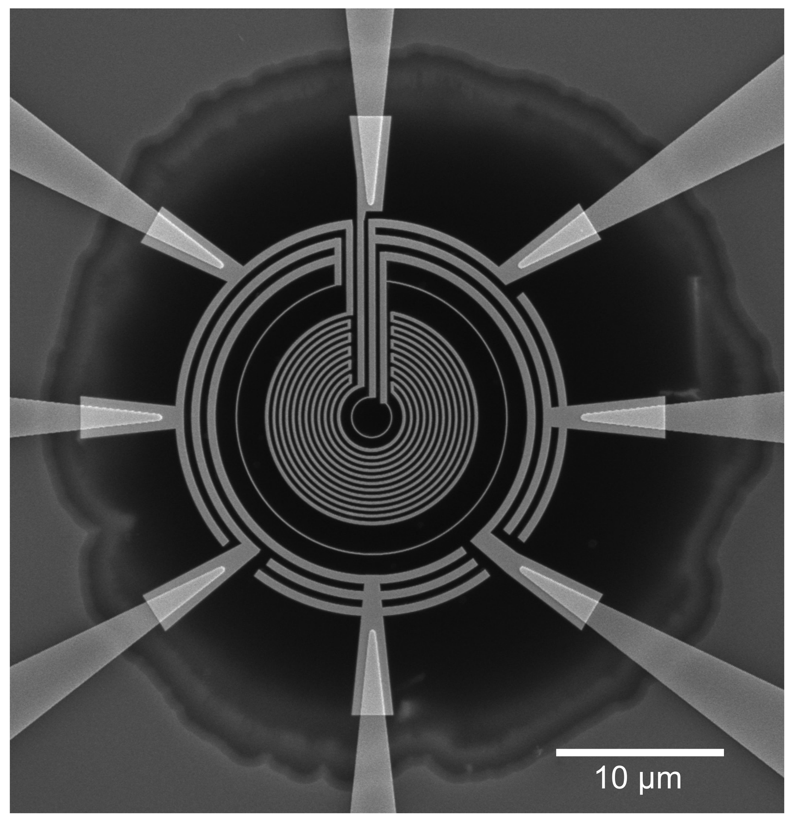
Possible layouts:

Optimize either for uniform temperature or varied temperature (and gradient effects).



Heater Design and Calibration: Simulation and experiment

Pt resistive heater localized to liquid on membrane to minimize image drift.

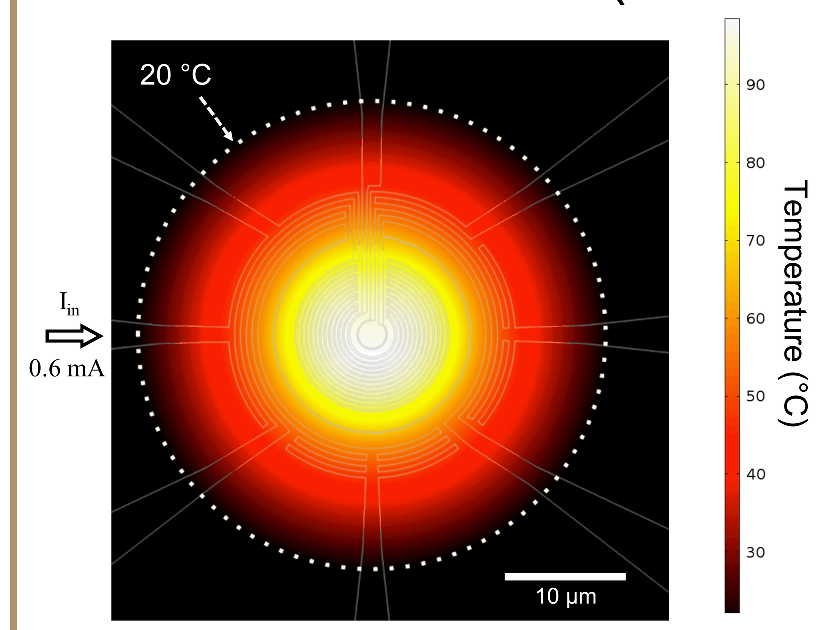


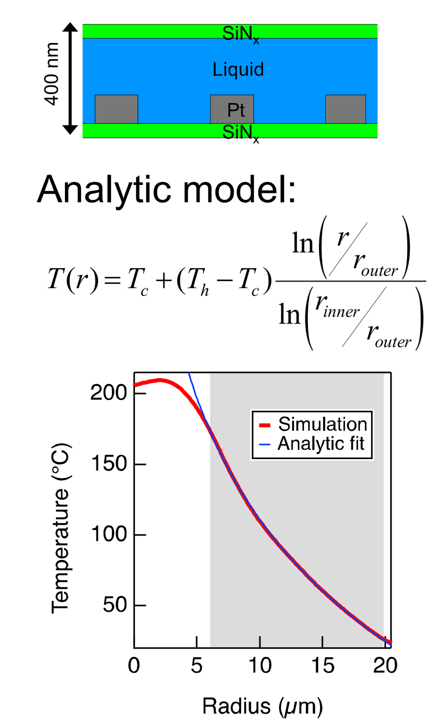
"Stovetop" design.

Details:
Patterned Pt lines, 40 nm thick,
Line width 150-200 nm.
Resistance 1-20 kΩ,
Current <1 mA.
Serpentine voltage drop about 5 V.
Insulated with ALD Al_2O_3.

Resistive thermometers inside and outside heater.

Temperature profile calculated using finite element simulation (COMSOL).

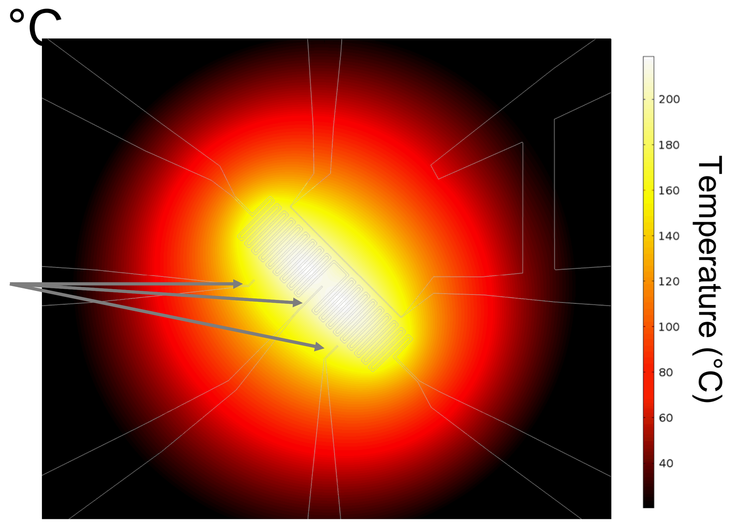




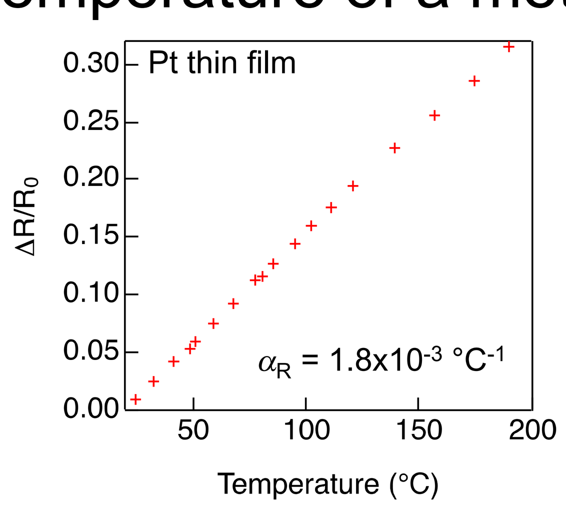
Excellent temperature uniformity in center, approximately 5 °C.

"Echem" design.

Various electrodes are exposed to different temperatures.



Resistive thermometry measures the temperature of a metal thermometer.



$$\frac{\Delta R}{R_0} = \alpha_R \Delta T$$

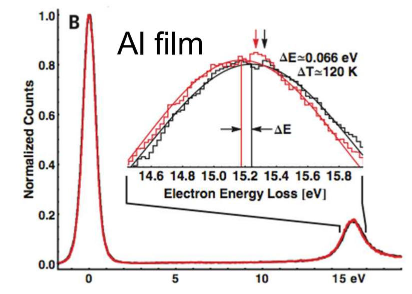
Gives an *average* temperature of the patterned thin-film resistor, not specifically the liquid.

Also enables calorimetry!

Measuring Liquid Temperature: Liquid metal plasmon thermometry

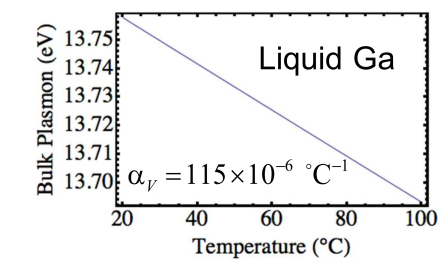
Knowing the **liquid** temperature is critical but nontrivial to measure.

Our technique: fill the cell with a liquid metal (Ga) and measure the bulk plasmon shift due to thermal expansion.



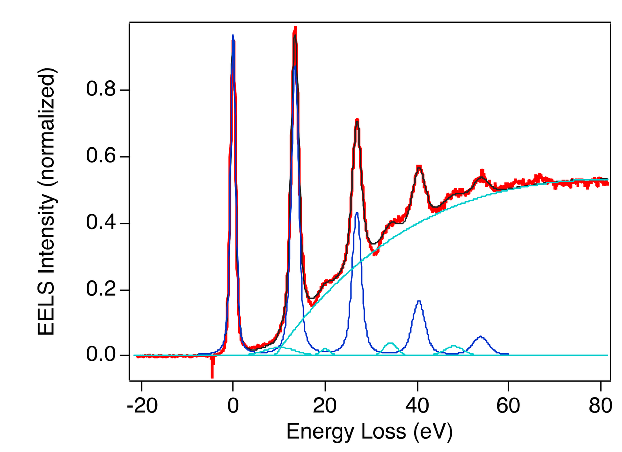
$$E_p = \sqrt{\frac{\hbar^2 e^2 n}{m\varepsilon_0}} \propto \sqrt{\rho}$$

$$\rho = \rho_0 / (1 + \alpha_V \Delta T)$$

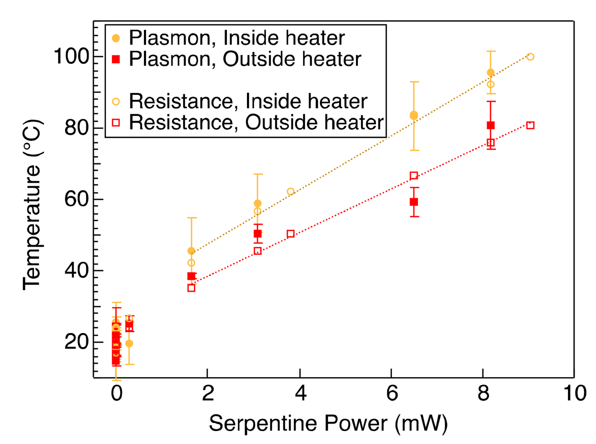


$$\frac{dE_p}{dT} = -0.81 \text{ meV/K}$$

Mecklenburg, M. *et al. Science* **347**, 629 (2015).

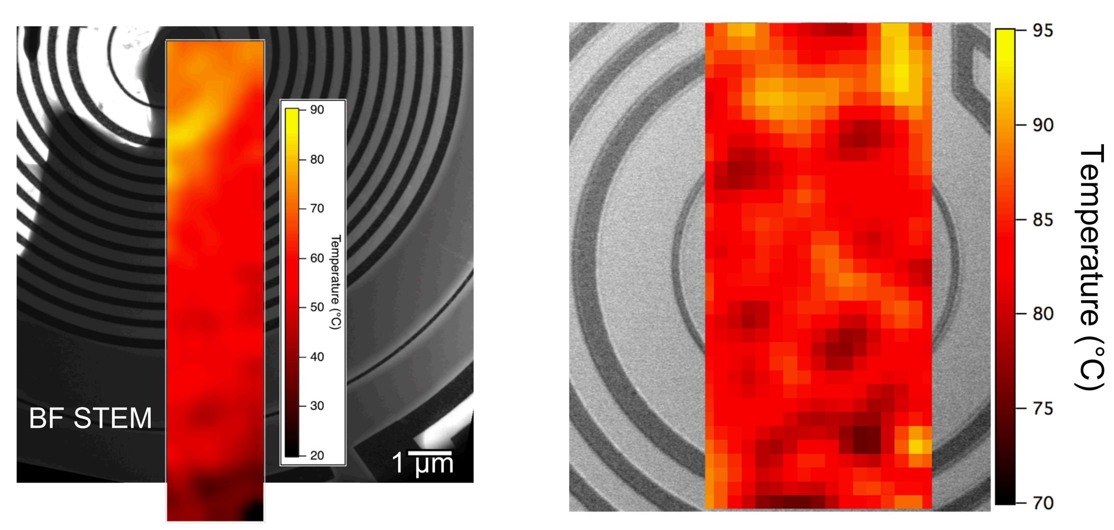


Example EELS spectrum of liquid Ga in liquid cell. Multipeak fitting used to find E_p.



Resistance and plasmon thermometry agree well.

Heat map can be generated by EELS mapping in Ga while heating:



Temperature fairly uniform in center, given a measurement technique accuracy of order 10 °C.

Conclusion

Patterning a thin film, serpentine resistive heater on the CINT liquid cell platform adds controlled temperature capability.

Combined simulation and experiment revealed the liquid temperature profiles.

Quantification was done with liquid metal, and results can be translated to conventional liquids.

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NANOSTRUCTURES for ELECTRICAL ENERGY STORAGE