PURDUE UNIVERSITY
Discovery Park

Electrical Thin Double Layer Simulation and Micro-electrochemical Supercapacitor Cooling

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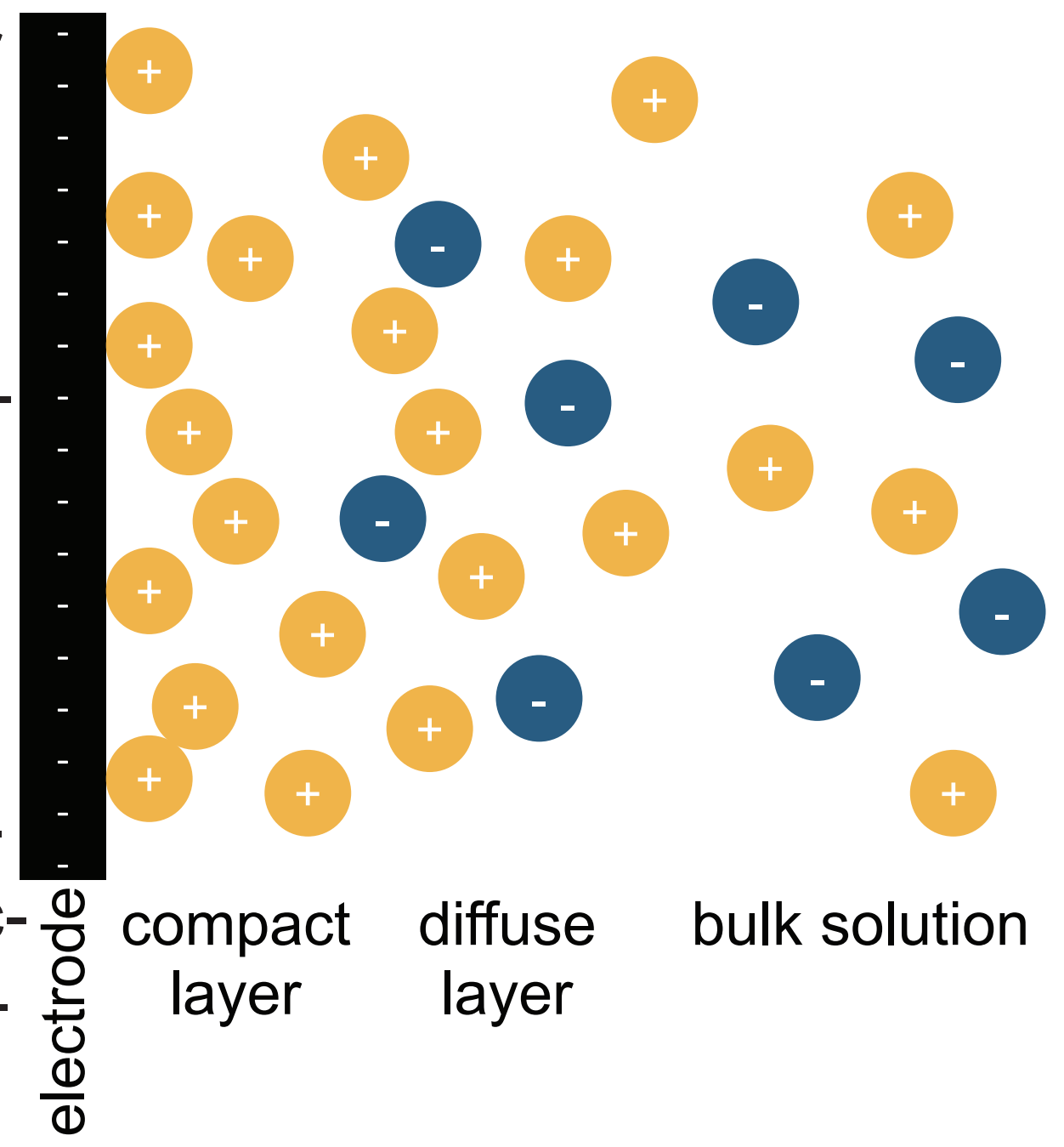
Background and Motivation

Deteriorating air quality has led to a growing need for rechargeable micro-power sources, such as energy sources for acceleration in hybrid-electric vehicles. The high energy density of electrochemical micro-supercapacitors (high surface area electrodes, covered with an electrolyte) has led to increased attention from the engineering and researching communities. In order to better understand the underlying mechanism of supercapacitors, a model to predict their behavior is needed. The first step in creating this model was to construct a description of the effect of electrolyte properties on the behavior of electrical thin double layers.



The components of the micro-supercapacitors (μSCs) used in this study were graphitic petal electrodes with a Ti/Au covering on a SiO_2 base, soaked in a PVA and H_2SO_4 polymer gel or aqueous electrolyte.

An electrical thin double layer (EDL) forms when a voltage is applied to a solid immersed in an aqueous electrolyte. It consists of two thin quasi-equilibrium layers of ions, first a compact or condensed layer of mostly counterions and then a diffuse layer of co- and counterions [1] (see figure above). This is similar to the electrodes in a μSC with a few simplifying assumptions, such as a flat electrode surface.

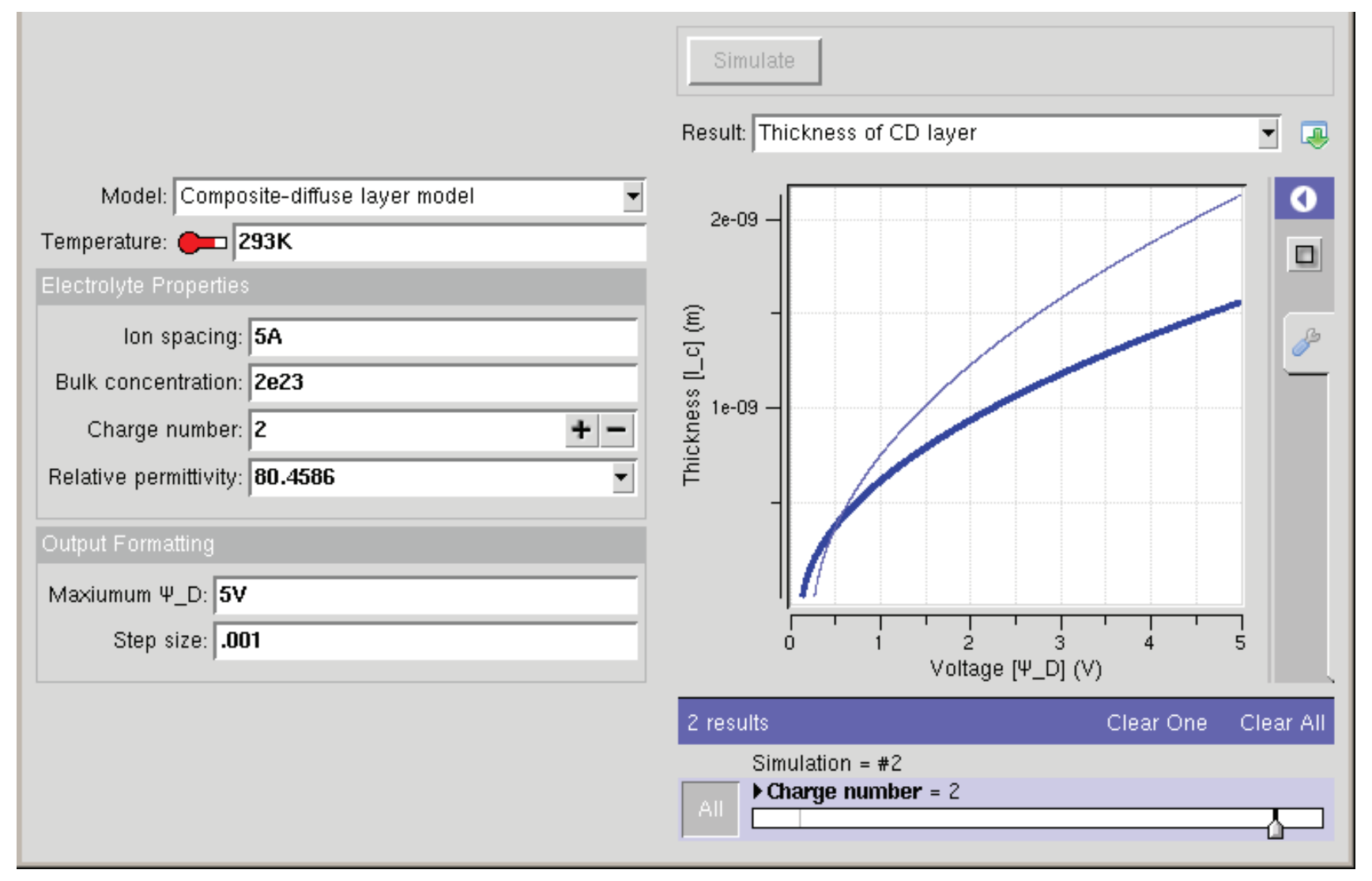
Three different models of EDLs were studied. The Poisson-Boltzmann equation (PB) is the most simplistic. It breaks down under very small applied potentials (potential must be small enough that the compact layer is only one layer of ions deep), and does not account for finite ion volume (steric effects). This is compared to a modified version of the Poisson-Boltzmann equation (MPB) and a composite-diffuse layer model (CDL), both of which account for steric effects. Using the CDL model, the transition from the condensed to the diffuse layer is sharply defined. This distance is defined as l_c [1].

Objectives

- ► To determine how electrolyte properties affect supercapacitors
  - ◊ To determine how electrolyte properties affect thin double layers
  - ◊ To relate thin double layers to supercapacitors
- ► To create an easy-to-use nanoHUB tool that demonstrates electrolyte property effects above
- ► To predict supercapacitor entropy generation and cooling, using above simulation

Results and Discussion

Simulation

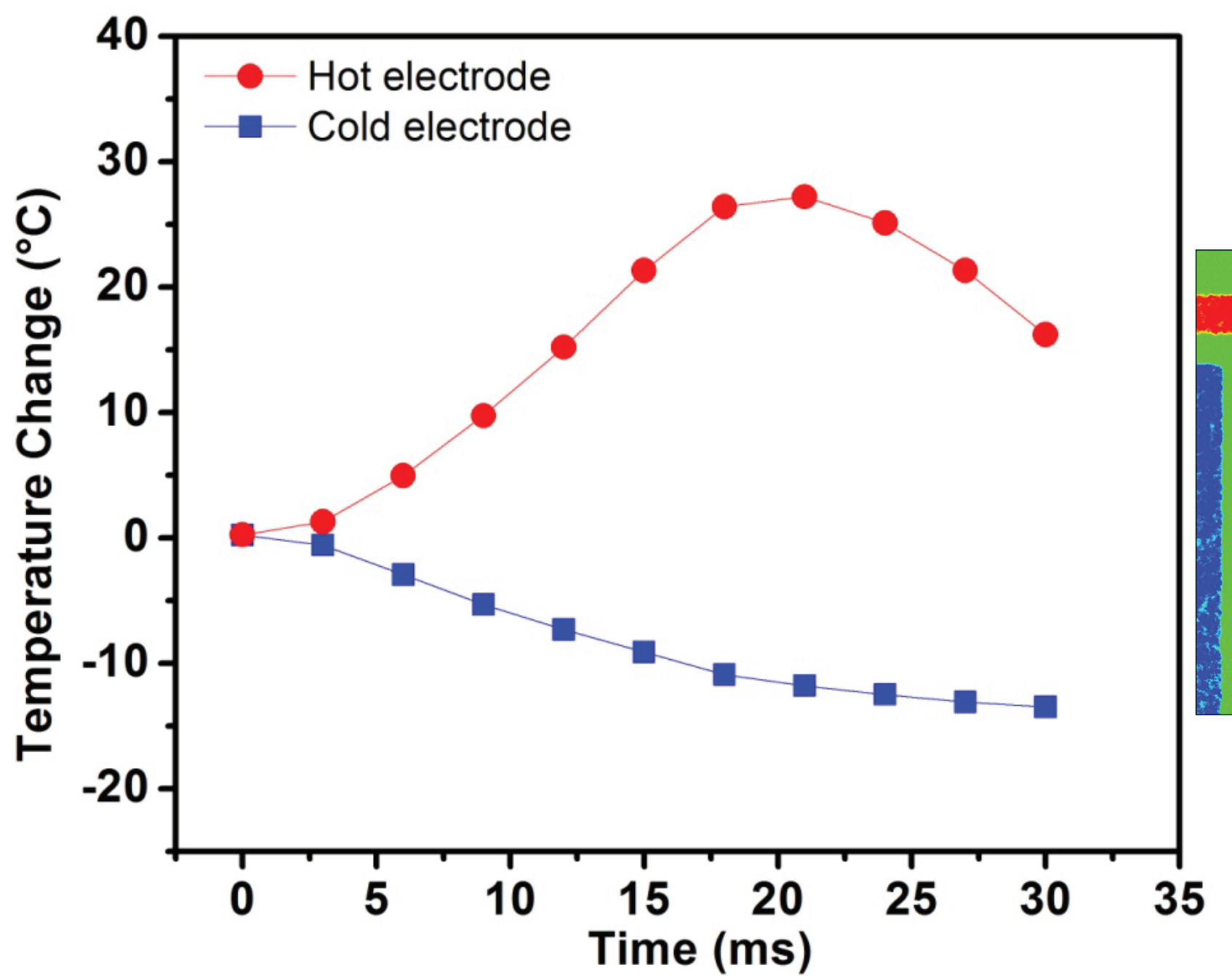


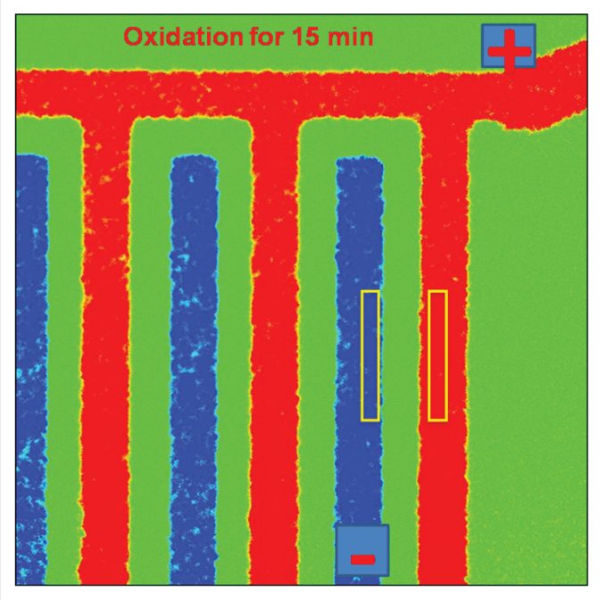
Result: Thickness of CD layer
Model: Composite-diffuse layer model
Temperature: 293K
Electrolyte Properties
Ion spacing: 5A
Bulk concentration: 2e23
Charge number: 2
Relative permittivity: 80.4586
Output Formatting
Maxiumum Ψ_D: 5V
Step size: .001
2 results
Simulation = #2
Charge number = 2

This is the tool interface that will be posted on nanoHUB displaying a sample output plot. For detailed output, see figures at right.

The plots to the right show how electrolyte properties affect behavior of electric thin double layers.

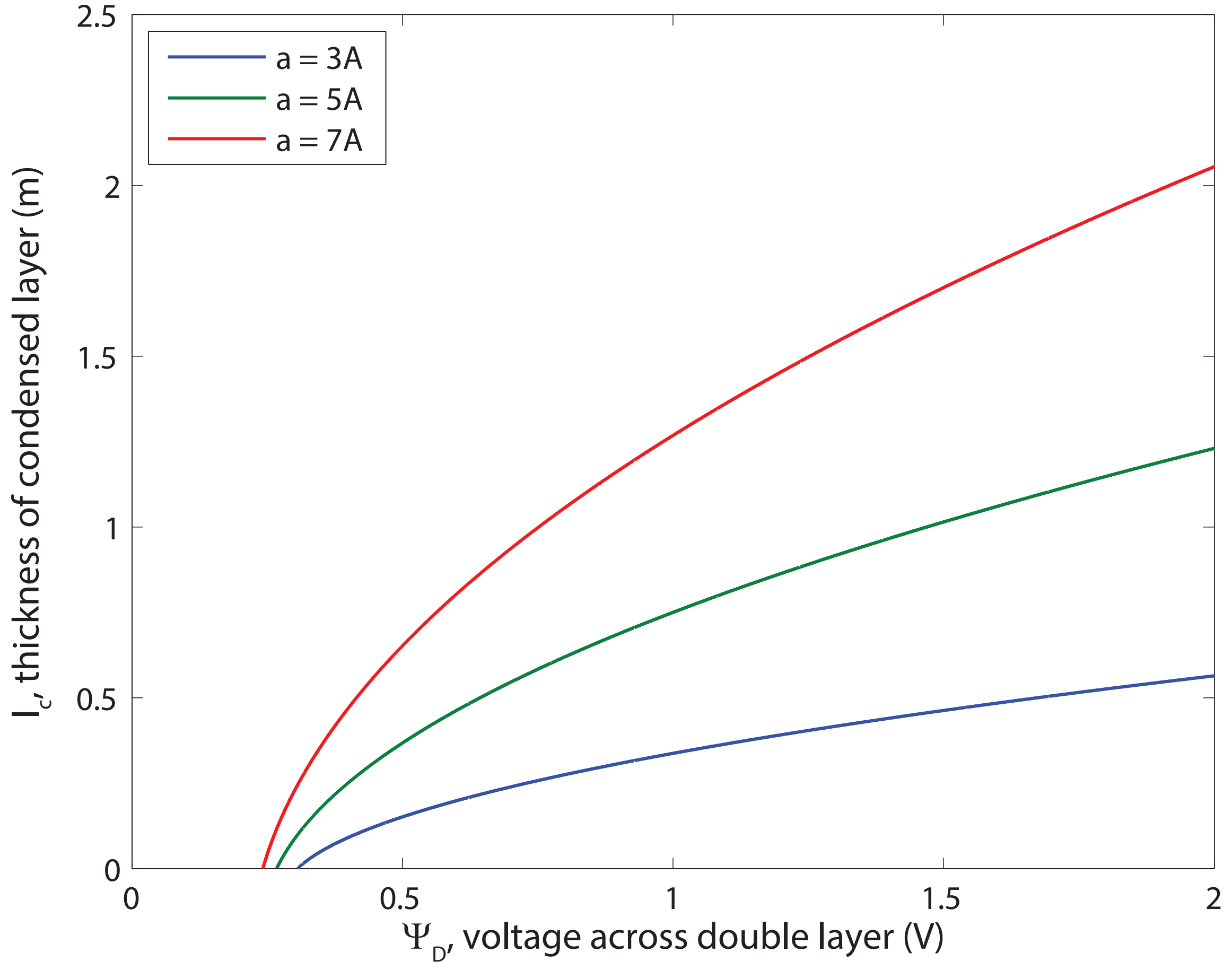
Experimental





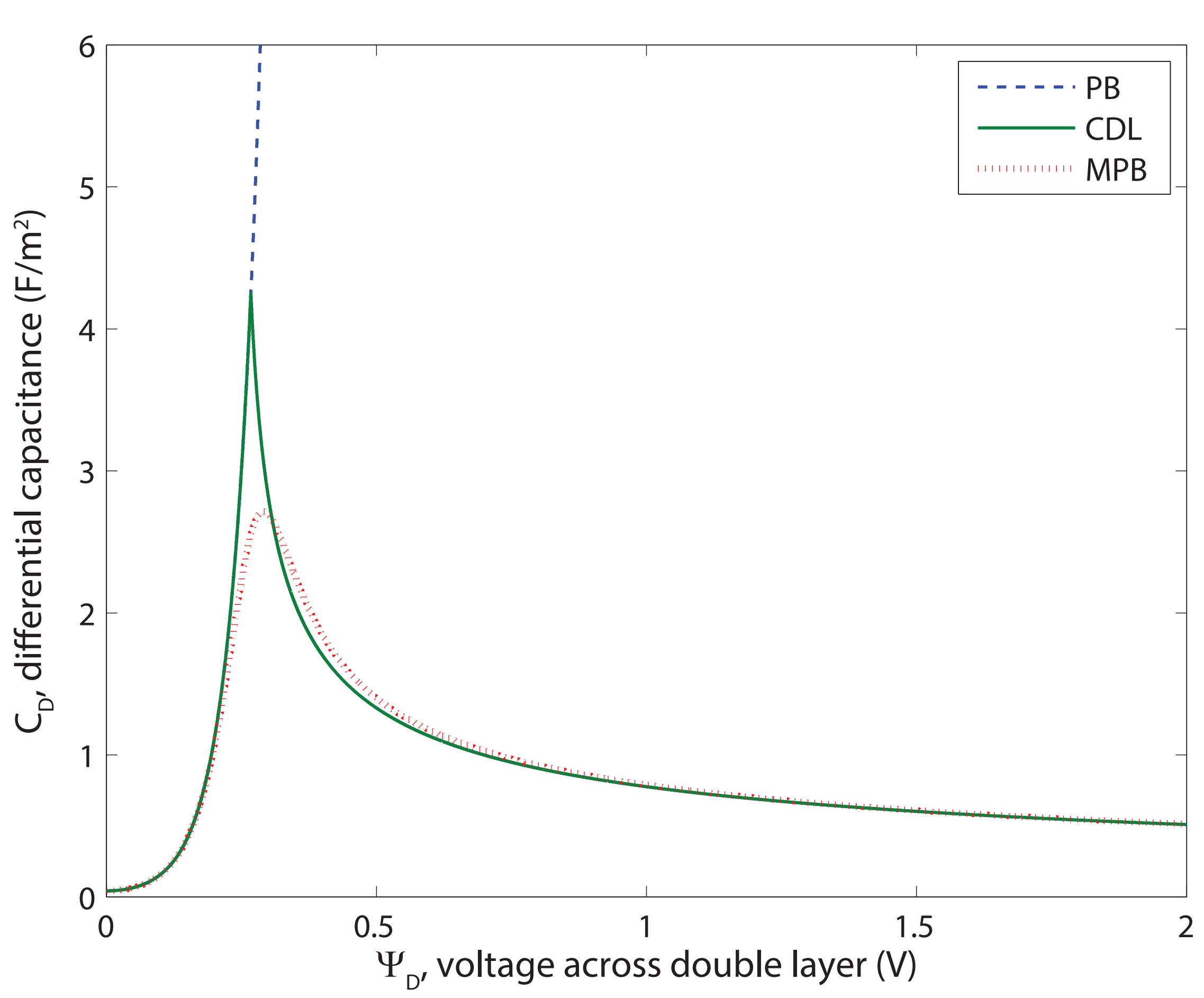
The thermoreflectance measurements showed unexpectedly high cooling in the negative electrode. The temperatures in the plot above were averaged over the boxed in area in the figure to the right. Data points were collected every 3 ms. Each point is the average of 3000 cycles.

Condensed Layer Thickness vs. Applied Voltage

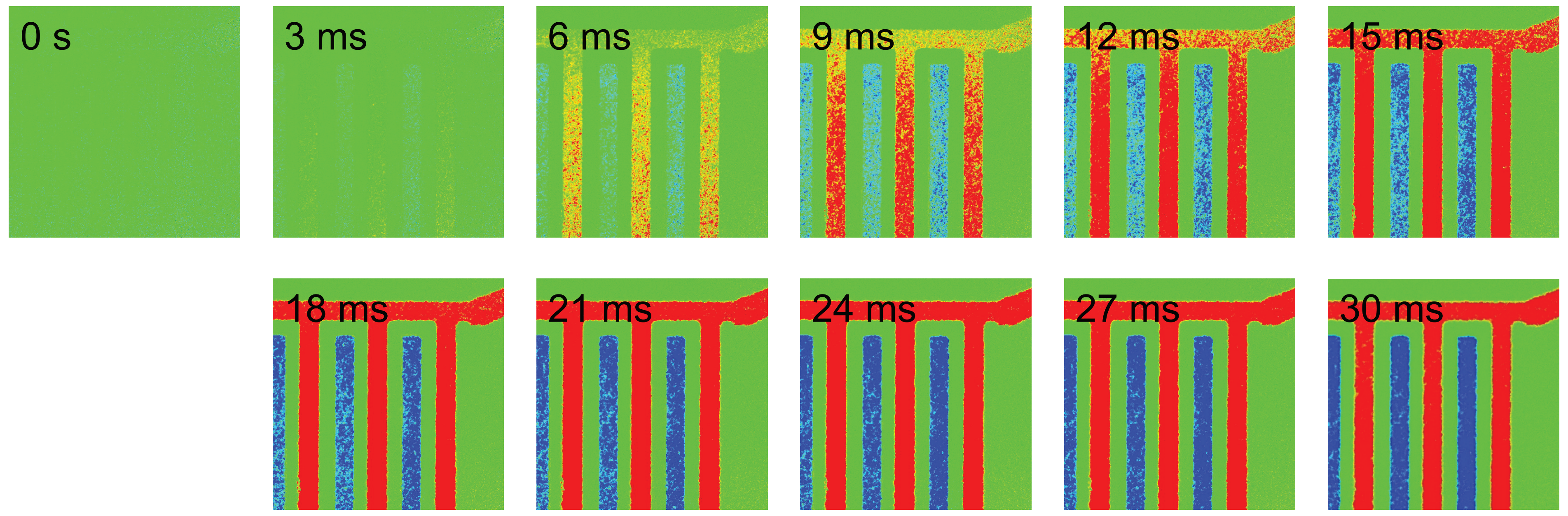


l_c is the thickness of condensed layer of counterions created when using CDL model. It is graphed for different ion spacing (a).

Differential Capacitance vs. Applied Voltage



Differential capacitance (C_D) is dq/ $d\Psi_D$ where capacitance is q/ Ψ_D. C_D is graphed for each model.



The photos above show a time lapse of the μSC charging and discharging under the applied voltage waveform shown in the Methods section. The red represents an increase in T and the blue represents a decrease in T.

Methods

Simulation

- ► Derived PB, CDL, and MPB equations [1]
- ► Created MATLAB code
- ► Compared dimensionless results to previous research [1]
  - ◊ Ex. l_c/λ_D vs. ze $|\Psi_D|$ / kT
- ► Re-dimensionalized equations
  - ◊ Ex. l_c vs. Ψ_D
- ► Created user interface in Rappture (xml) and integrated MATLAB code
- ► Published on nanoHUB.org

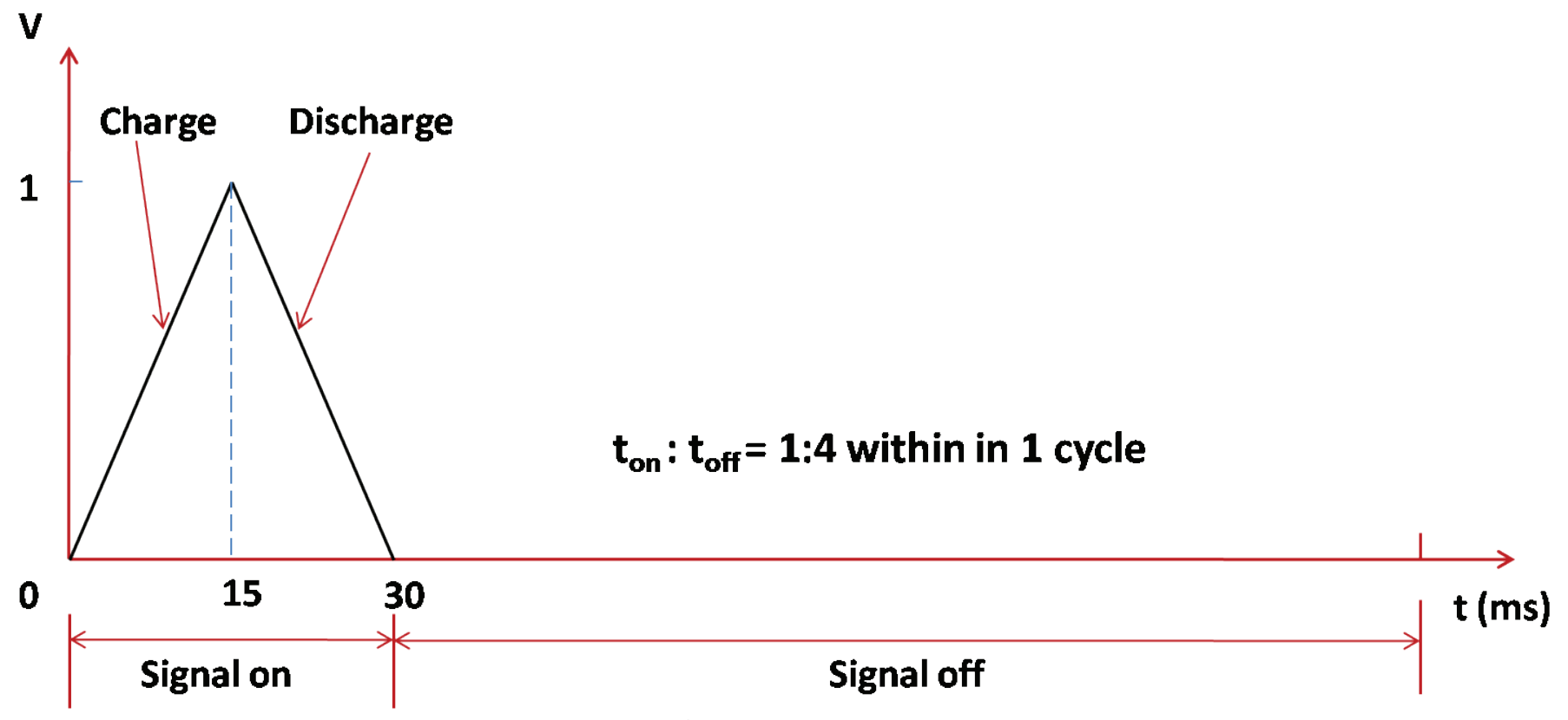
Experimental

Sample creation:

- ► Graphene petals were grown using microwave plasma chemical vapor deposition
  - ◊ SiO_2 base, approximately 15 mm x 6 mm x 2 mm
  - ◊ Plasma power = 600 W for 30 minutes
- ► Sheets were shaped into an interdigitated configuration using photolithography
- ► Petals were covered with a 600 nm layer of Ti/Au for enhanced light reflectance and then oxidized for 15 min
- ► Electrodes were soaked in an electrolyte
  - ◊ Aqueous: 1 M H_2SO_4 in H_2O, or
  - ◊ Solid state polymer gel: H_2SO_4 in PVA

Thermoreflectance measurements:

- ► Used system of wide-field LED illumination and CCD camera to capture thermal data
- ► Must use polymer gel electrolyte, ripples in aqueous create extremely high noise level
- ► Performed a base measurement with device off to capture background noise
- ► Applied 0-1 V voltage waveform shown below



- ► Took measurements for ≥2000 cycles and average measured temperature changes

Conclusions

- ► The EDL simulation shows several trends, such as:
  - ◊ Steric effects have a large impact, usually leading to opposite results of PB model [1]
  - ◊ Differential capacitance reaches a maximum then decreases when accounting for steric effects [1]
- ► The cause of the μSC cooling is still unknown, one possibility is the electrocaloric effect

Future work

- ► Find the cause of the cooling in μSCs
- ► [2] uses volume of condensed layer to calculate ΔS and from that ΔT in μSCs
  - ◊ Apply EDL model to to μSCs to find volume of condensed layer
  - ◊ Use that to calculate ΔT observed in experiments

References

[1] M. S. Kilic, M. Z. Bazant, and A. Ajdari, "Steric effects in the dynamics of electrolytes at large applied voltages. I. Double-layer charging," Physical Review E, vol. 75, p. 021502, 2007.

[2] J. Schiffer, D. Linzen, and D. U. Sauer, "Heat generation in double layer capacitors," Journal of power sources, vol. 160, pp. 765-772, 2006.

Acknowledgements

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