Ionic diffusion in laser-modified carbon-based porous supercapacitor electrodes

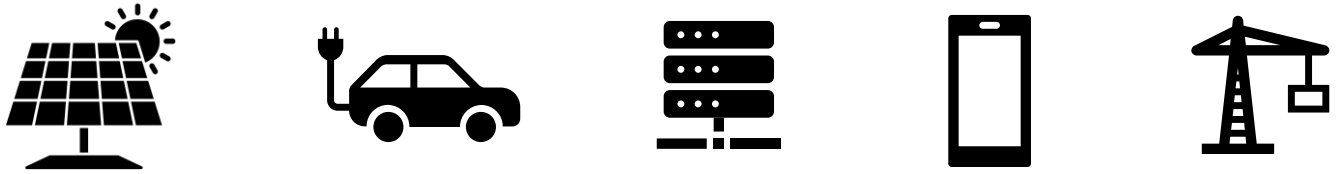
Baptista, J.M.[1, 2], Gaspar, G. [1], Santos, D.R. [1, 3], Silva, P. [4], Guerra, A. [1], Correia, J.P. [3], Wijayantha, U.K.G. [2] & Lobato, K. [1].

[1] Instituto Dom Luiz, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[2] Energy Research Laboratory (ERL), Chemistry Department, Loughborough University, Leicester LE11 3TU, United Kingdom
[3] Centro de Química Estrutural, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal
[4] Departamento de Engenharia Geográfica, Geofísica e Energia, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal

Symposium H – Laser material processing: from fundamental interactions to innovative applications

3rd June 2021

Why do we need supercapacitors?



John B. Goodenough, Chemistry Nobel Prize (2019) for Li-ion batteries

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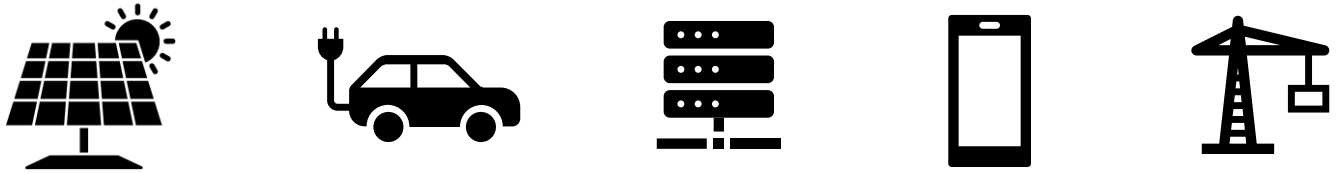

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… Because batteries are not good enough!

Why do we need supercapacitors?

vs

- ✓ High energy density (up to 270 Wh/kg [1])
- ✗ Low power density (< 680 W/kg [1])
- ✗ Low cyclability (< 3 000 cycles [1])

- ✗ Low energy density, E' (< 10 Wh/kg) [2]
- ✓ High power density (up to 80 kW/kg) [2]
- ✓ High cyclability (> 1 million cycles [2])

[1] K. Liu *et al*., "A brief review on key technologies in the battery management system of electric vehicles," *Front. Mech. Eng.*, vol. 14, no. 1, pp. 47–64, 2019.
[2] SkeletonTechnologies, "SkelCap Industrial Ultracapacitor Cells," 2020. [Online]. Available: https://www.skeletontech.com/skelcap-sca-ultracapacitor-cells. [Accessed: 20-May-2021]

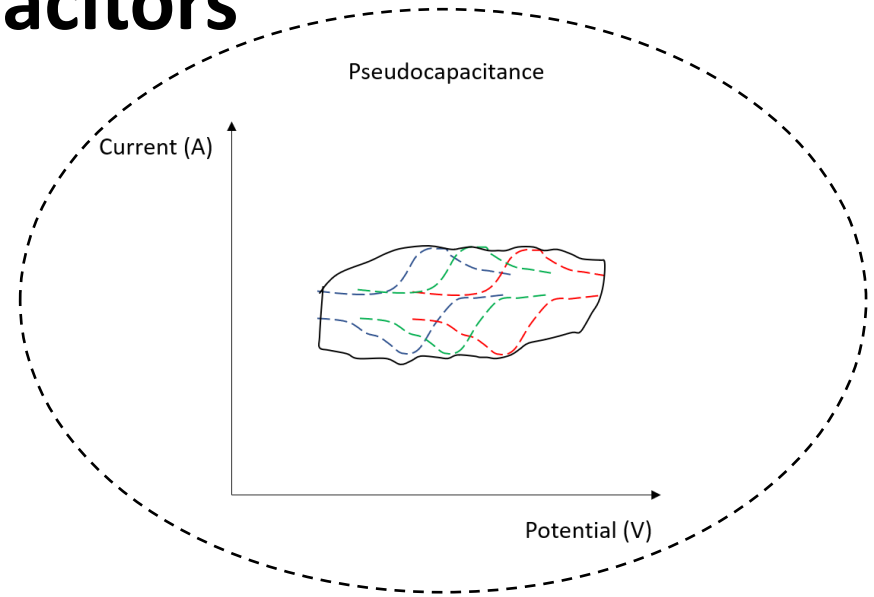
Main Challenge for Supercapacitors

specific capacitance

energy density

$$E' = \frac{1}{2} C' \Delta V^2$$

stable voltage range



Main Challenge for Supercapacitors

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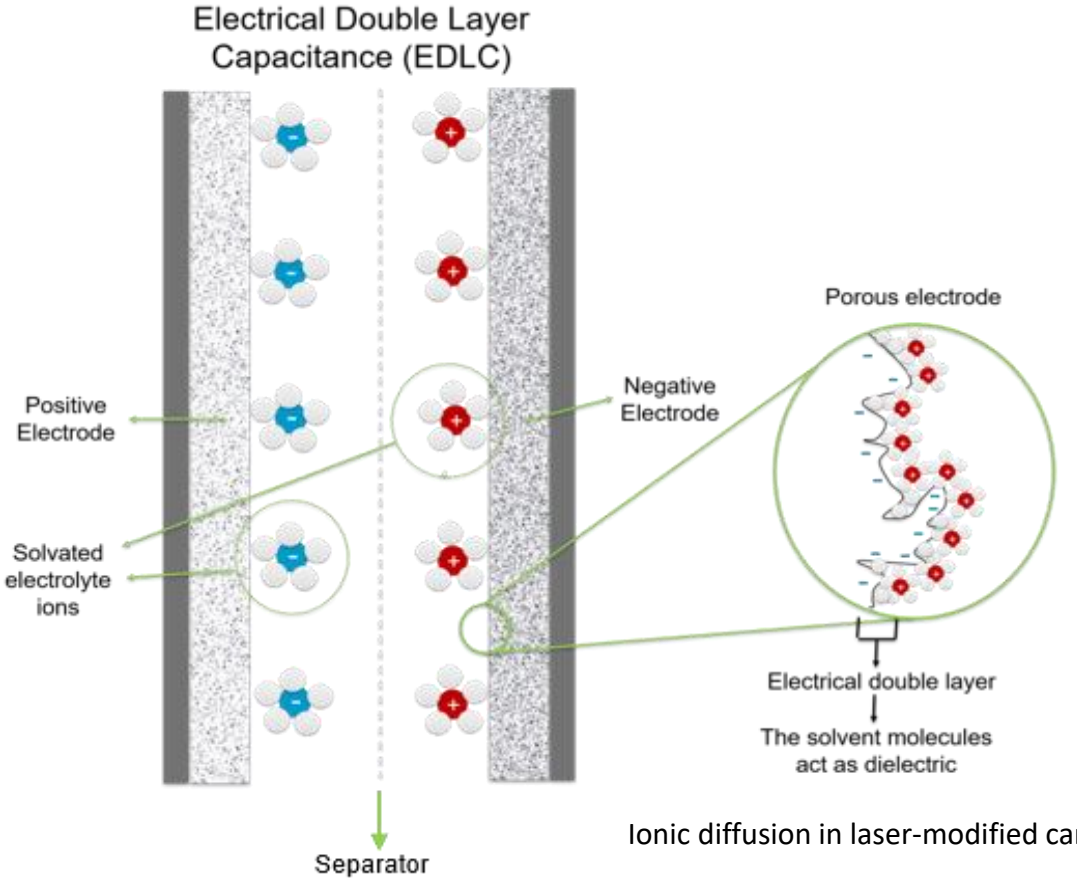
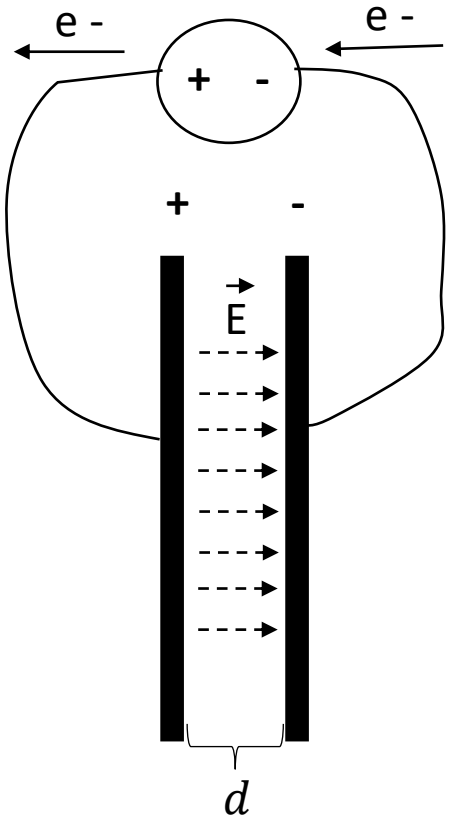




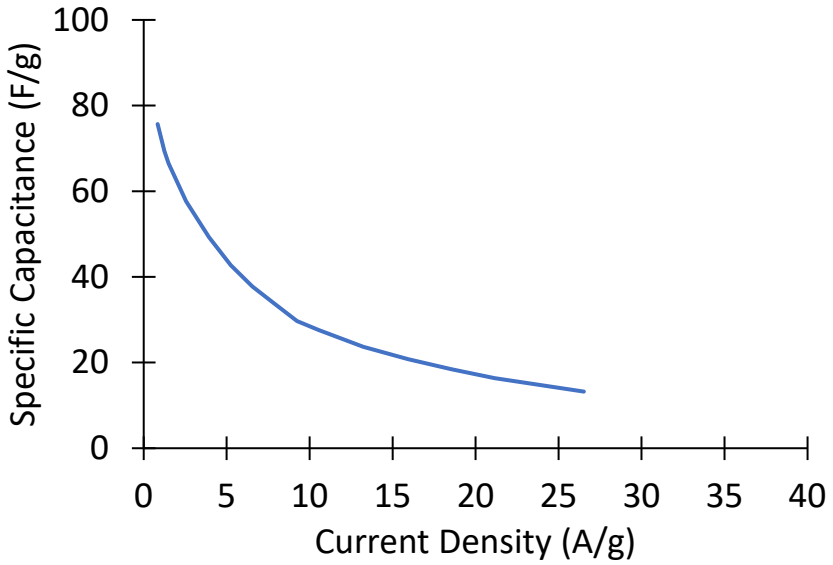
capacitance

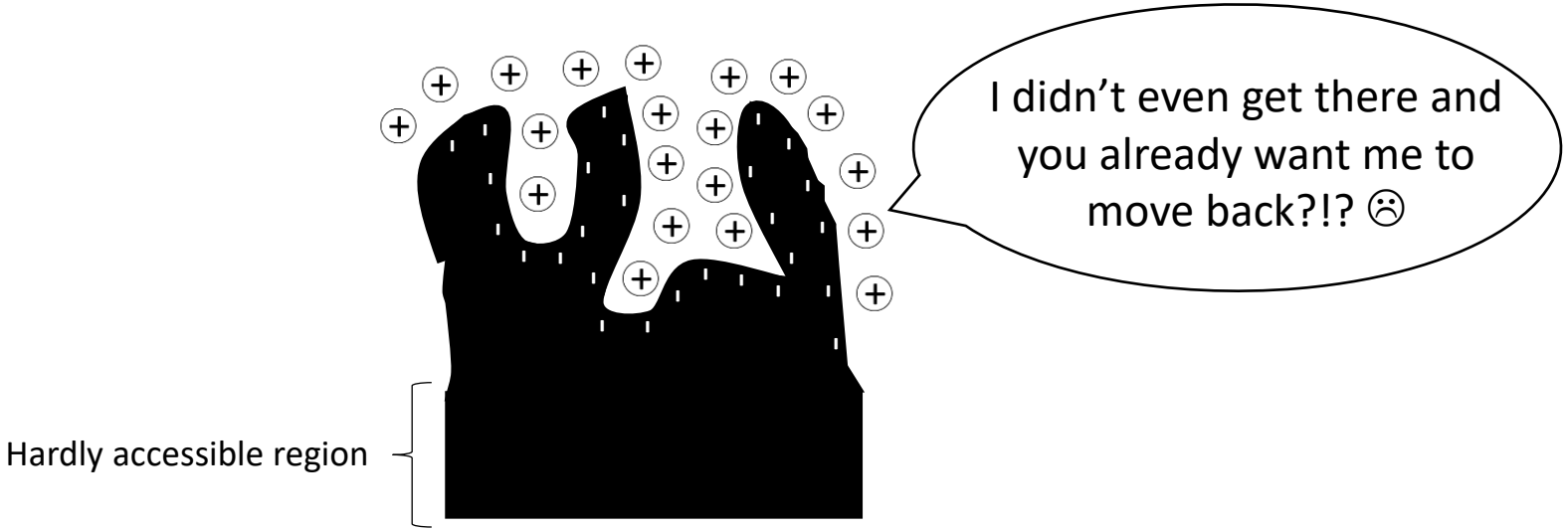
$$C = \frac{\int dQ}{\int dV}$$ → stored charge / → voltage

$$C = \varepsilon \frac{A}{d}$$ → **area**

electric permittivity of the dielectric

Laser Scribing Activated Carbon Electrodes





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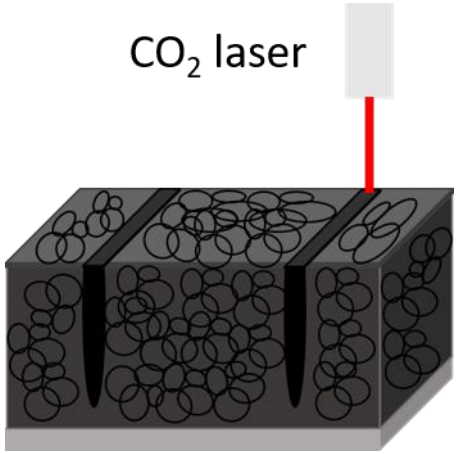
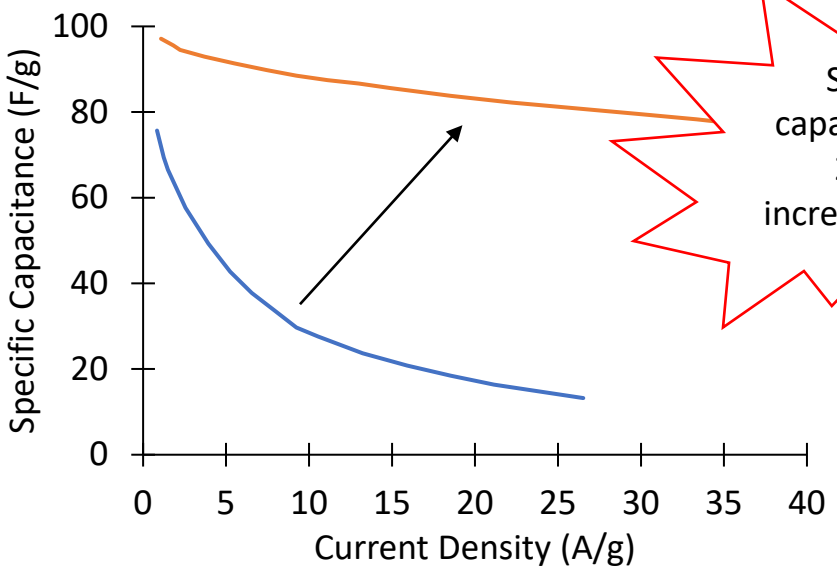
Next-Generation Activated Carbon Supercapacitors: A Simple Step in Electrode Processing Leads to Remarkable Gains in Energy Density

*Jee Y. Hwang, Mengping Li, Maher F. El-Kady, and Richard B. Kaner**

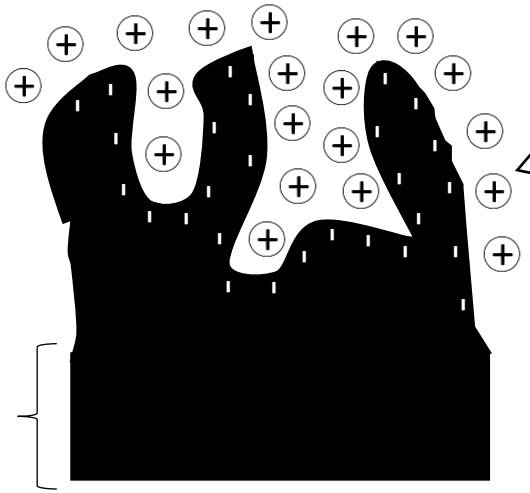


- ✓ Low-cost process
- ✓ Higher accessibility to inner parts of electrode

Laser Scribing Activated Carbon Electrodes



Specific capacitance at 25 A/g increased ca. 4x



Hardly accessible region

I didn't even get there and you already want me to move back?!? ☹

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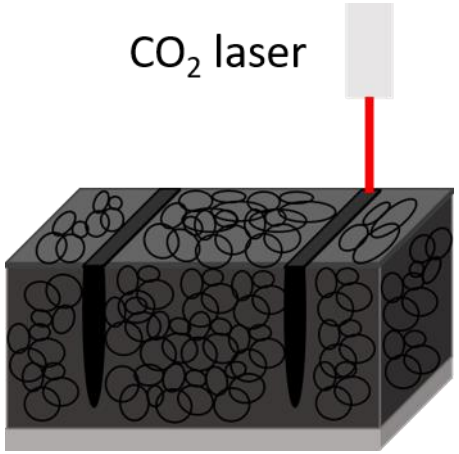

- ✓ Low-cost process
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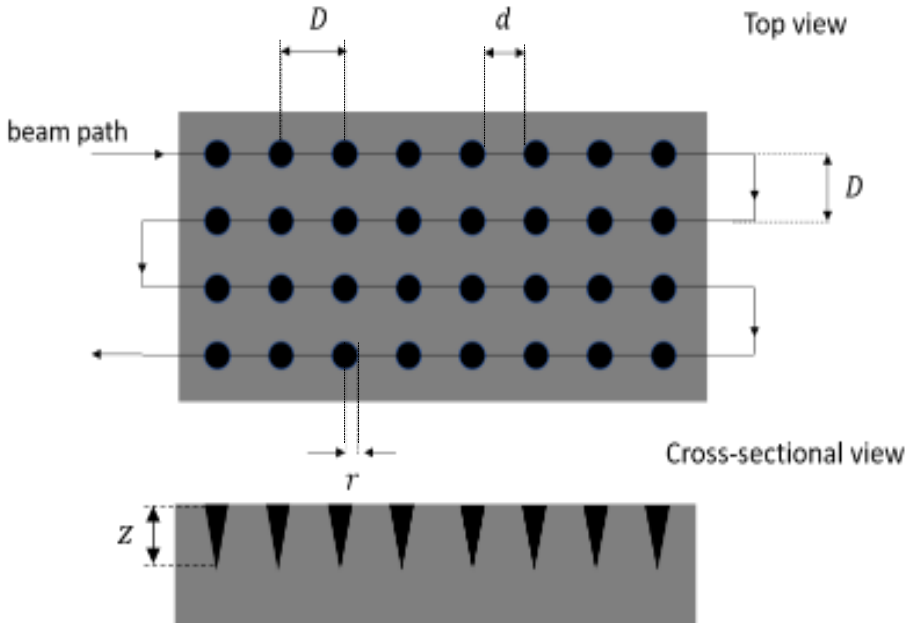
Laser Scribing Activated Carbon Electrodes

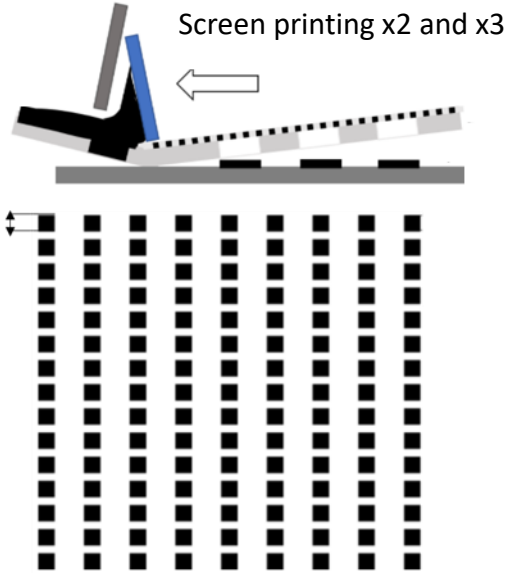


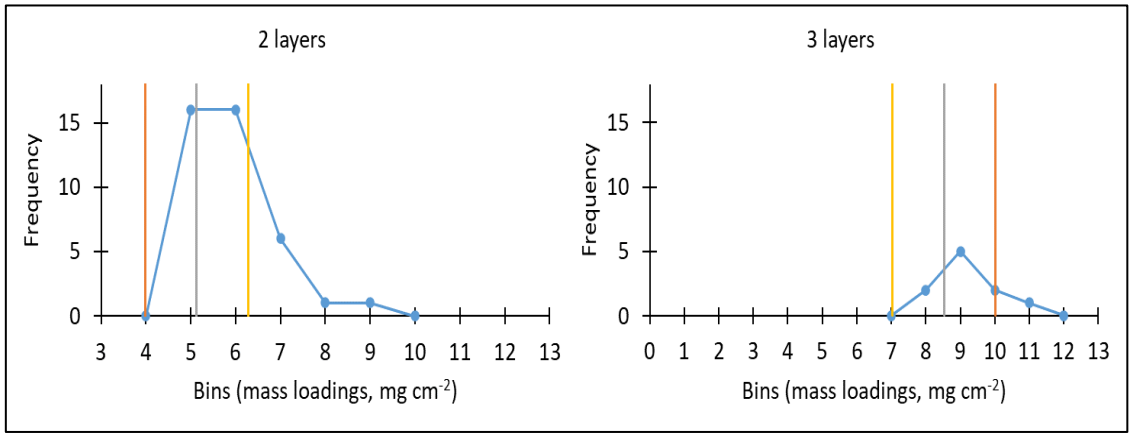
- d should be as small as possible ⟶ impact on mechanical stability?
- r should be as small as possible ⟶ beam size is ca. 42 µm
- z should be as large as possible ⟶ must be smaller than electrode thickness

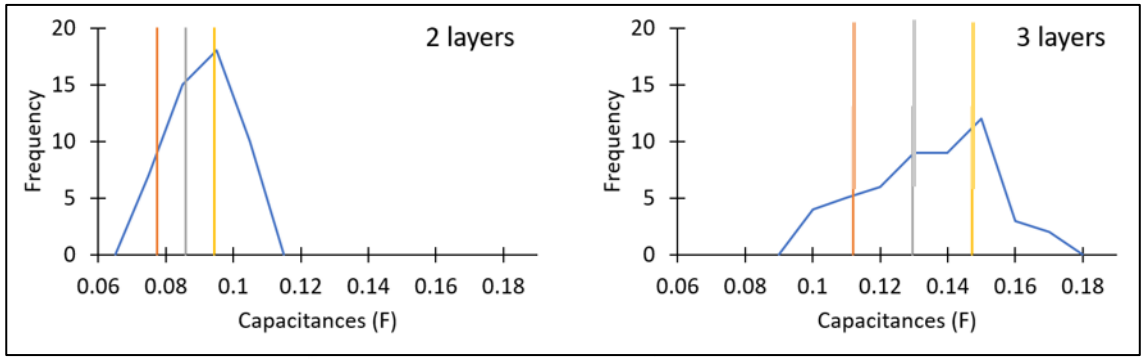
Tunable processing parameters:

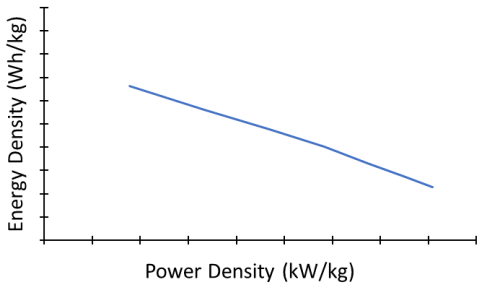
- **Raster speed (v)** ⟶ $D = \frac{v}{N_{\mathrm{pps}}}$ ⟶ **D = {100; 120; 140} µm**
- Number of pulses per second (N_{pps})
- **Average power (P_{avg})** ⟶ $E_{pulse} = \frac{P_{avg}}{N_{\mathrm{pps}}}$ ⟶ **E_{pulse} = {257; 314; 371} µJ**
- Wave Form ($\Delta t_{pulse} = 220\ ns; P_{peak} = 8\mathrm{kW}$)

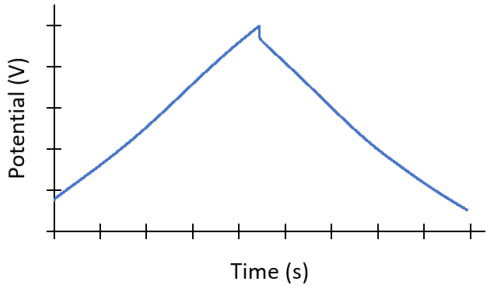
What we did

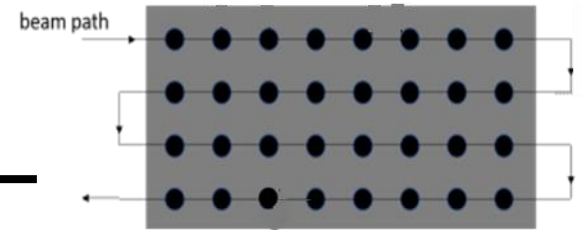






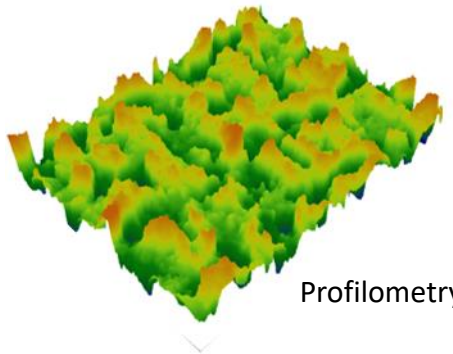




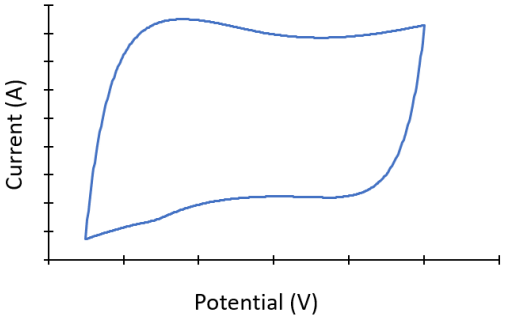


9 conditions for each thickness

$\begin{cases} D = \{100; 120; 140\}\ \mu m \\ E_{pulse} = \{257; 314; 371\}\ \mu J \end{cases}$

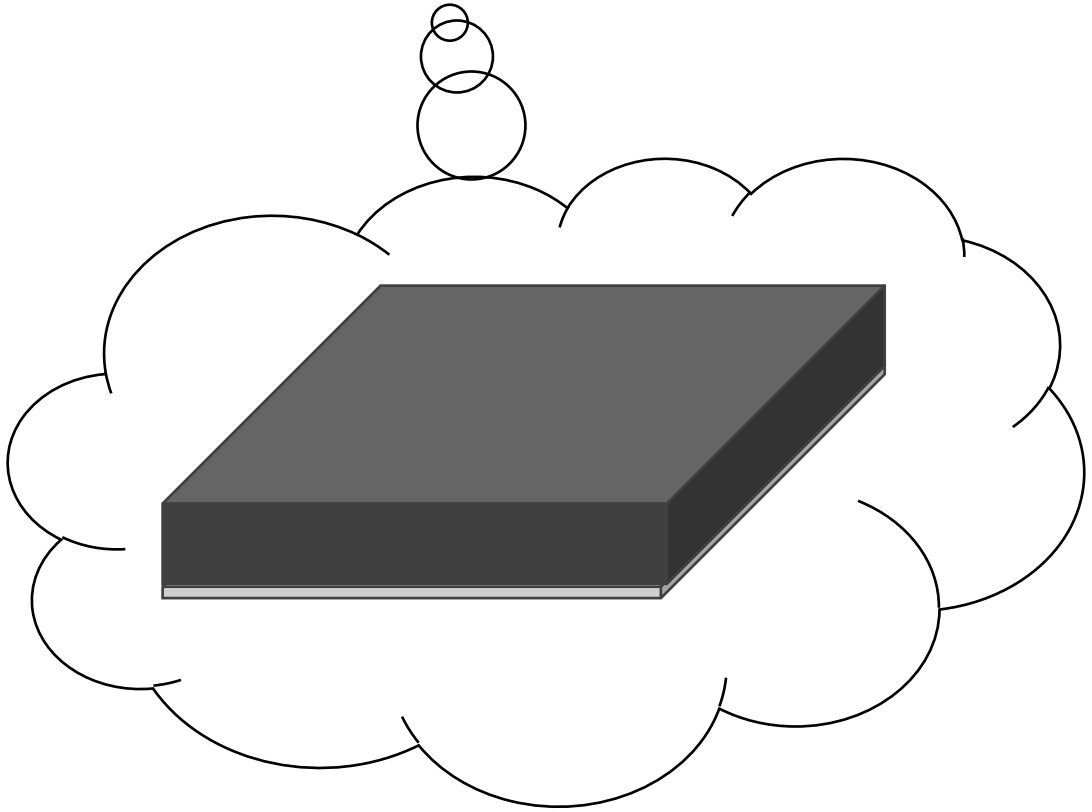


Profilometry

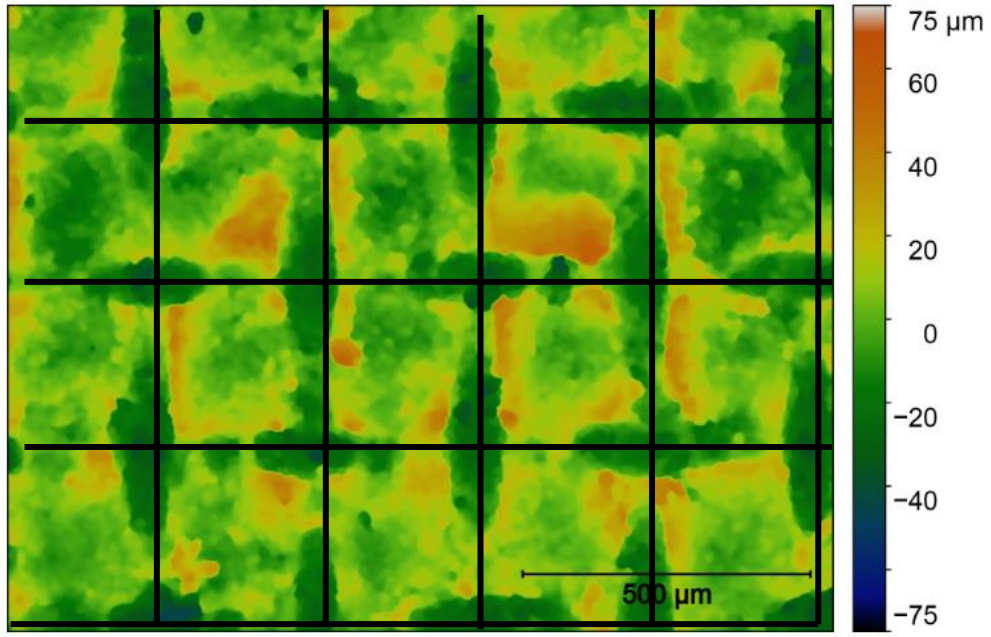


Results

What we thought we had…

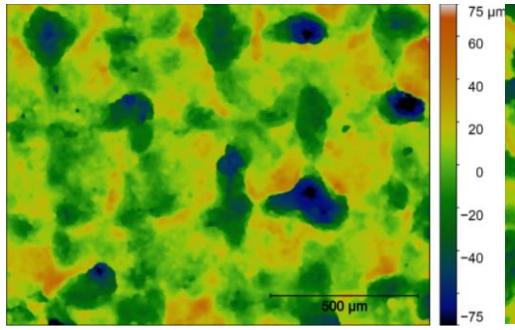


What we actually had

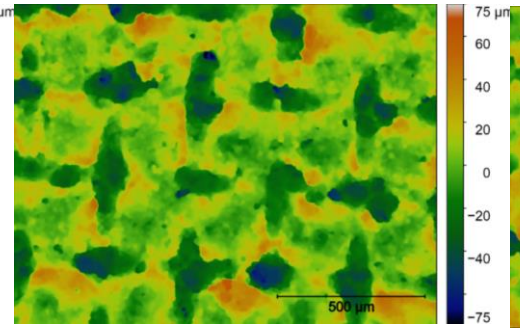


Results

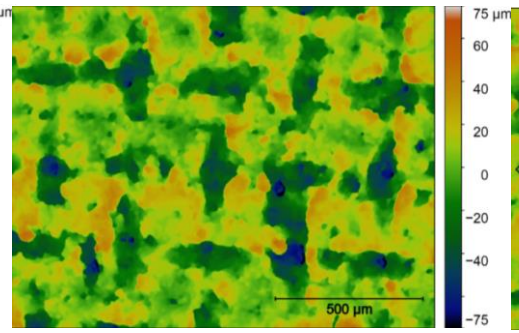
NLSAC 2L



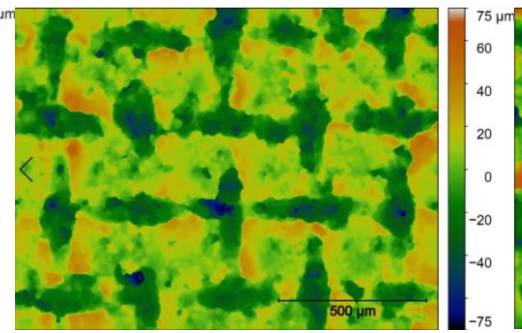
(257 µJ, 100 µm), 2L



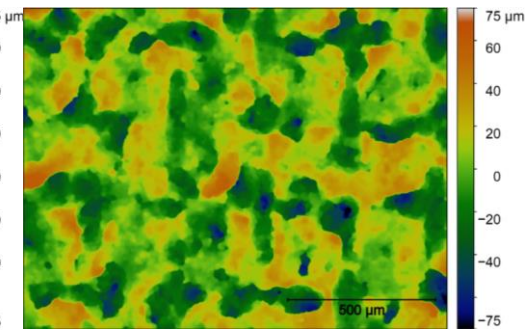
(371 µJ, 100 µm), 2L



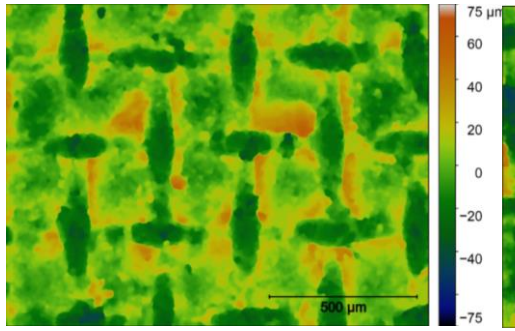
(371 µJ, 120 µm), 2L



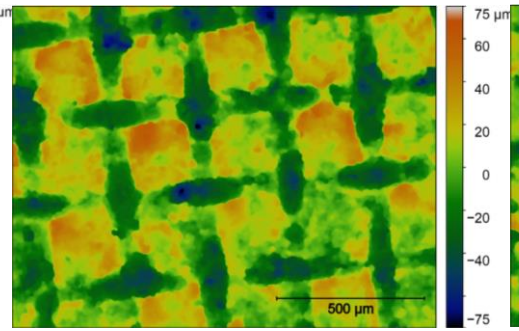
(371 µJ, 140 µm), 2L



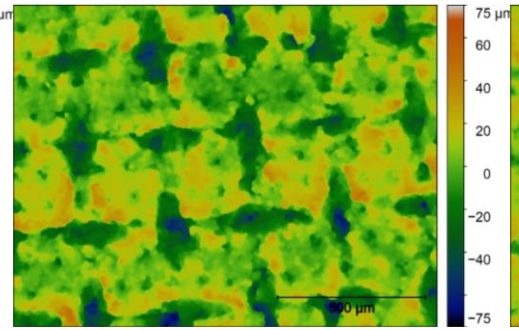
NLSAC 3L



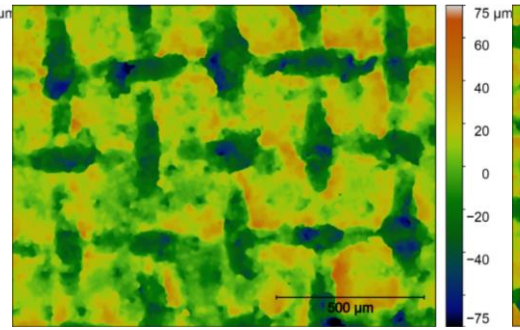
(257 µJ, 100 µm), 3L



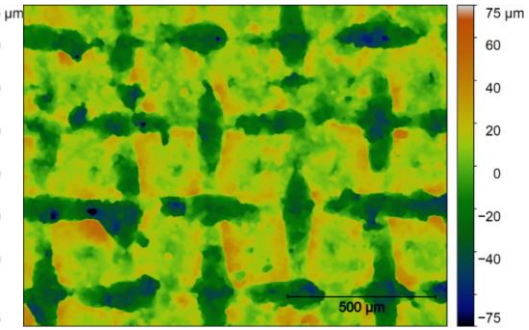
(371 µJ, 100 µm), 3L



(371 µJ, 120 µm), 3L

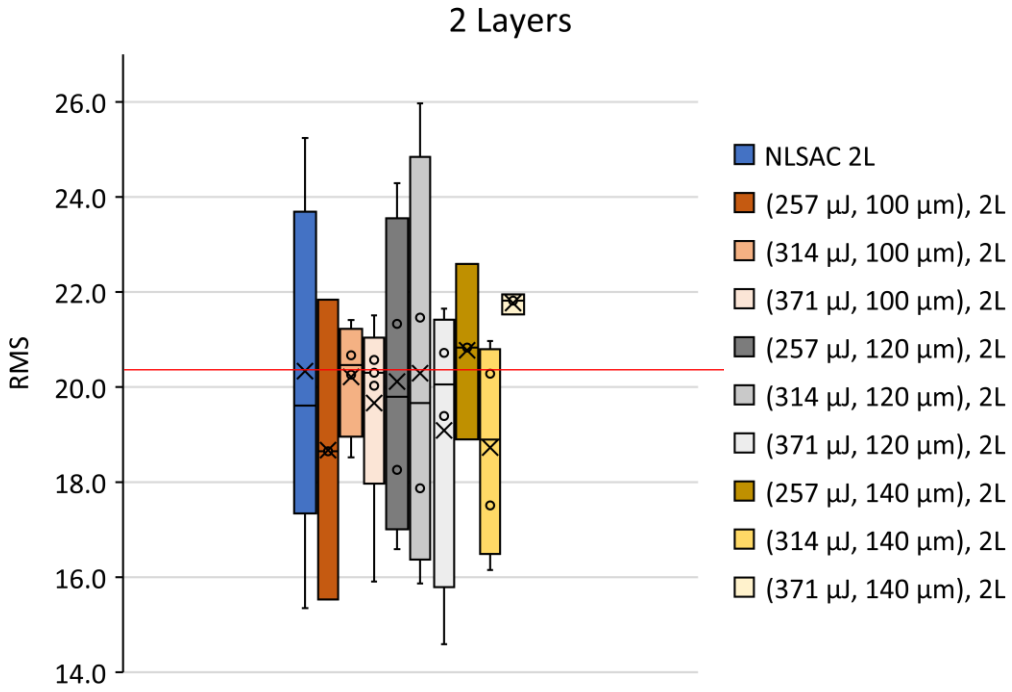


(371 µJ, 140 µm), 3L



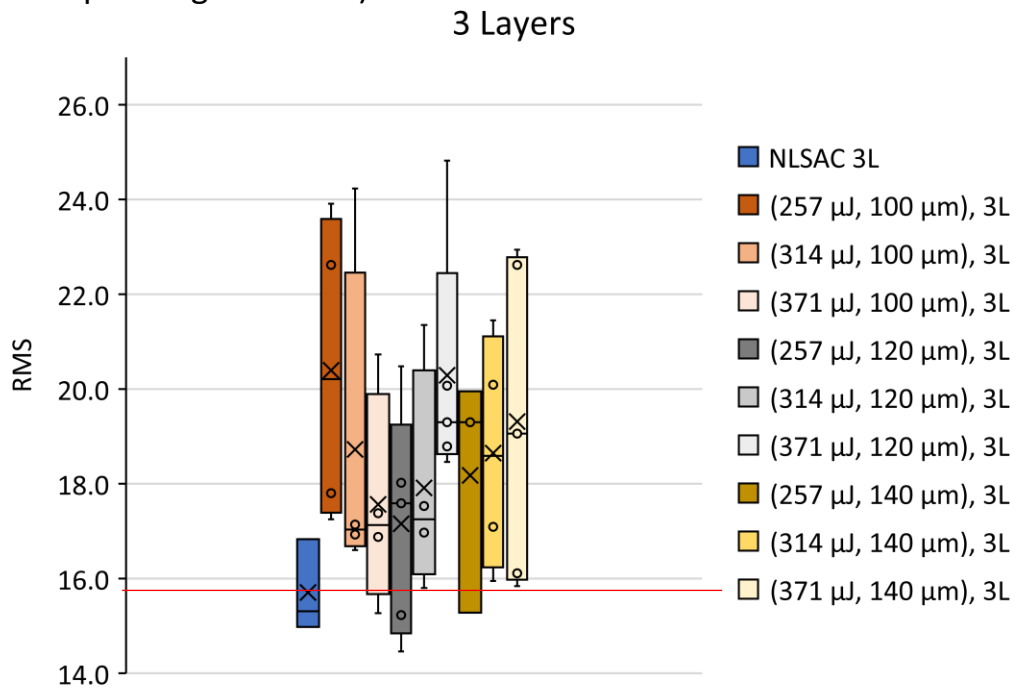
Results

- For the 2-layered electrodes, most of the laser-processed ones seem to have an RMS roughness very similar to that of the non-laser scribed electrodes

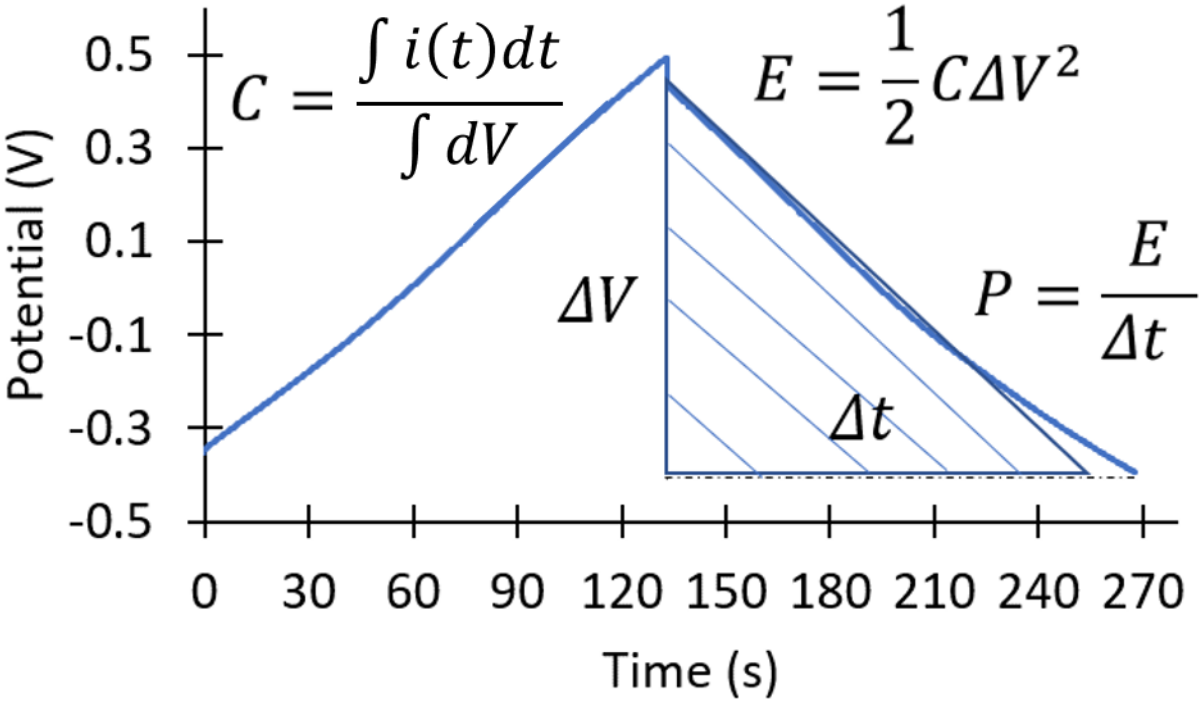


- The 3-layered electrodes seem to have a lower RMS than the 2-layered electrodes but laser-processing seems to increase its value.

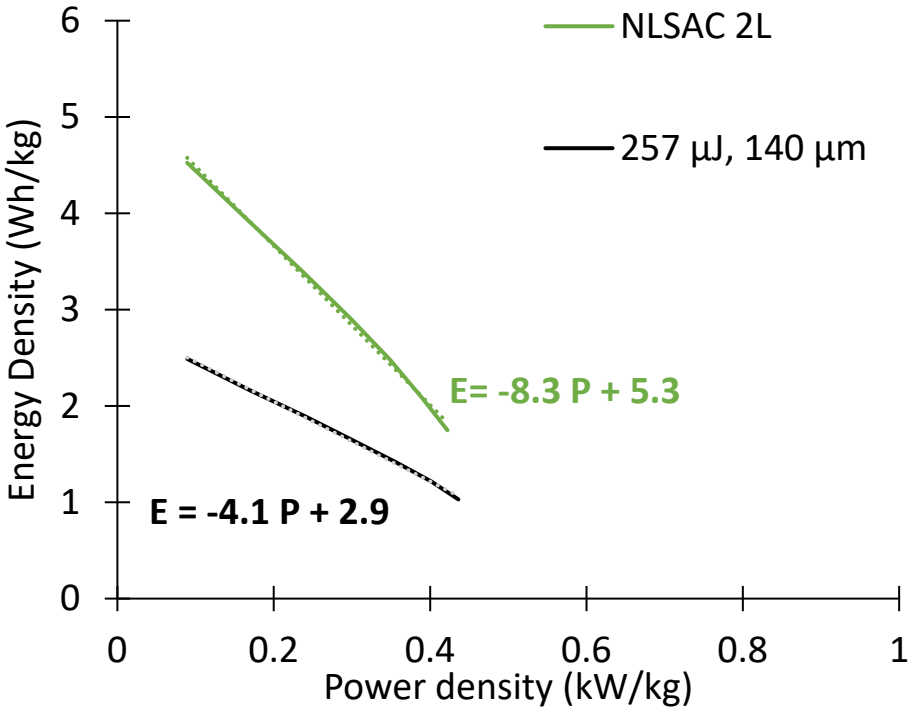
- For a 120 µm and a 140 µm spacing, the RMS increases with power; the opposite happens for 100 µm (possibly due to the collapse of the walls separating the holes)

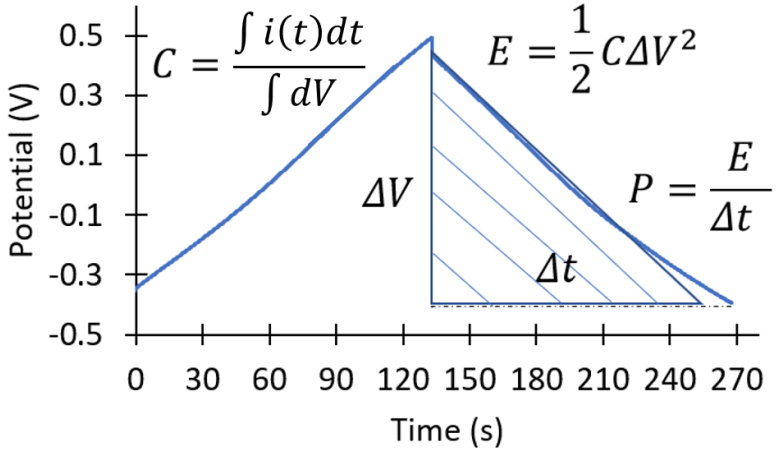


Results

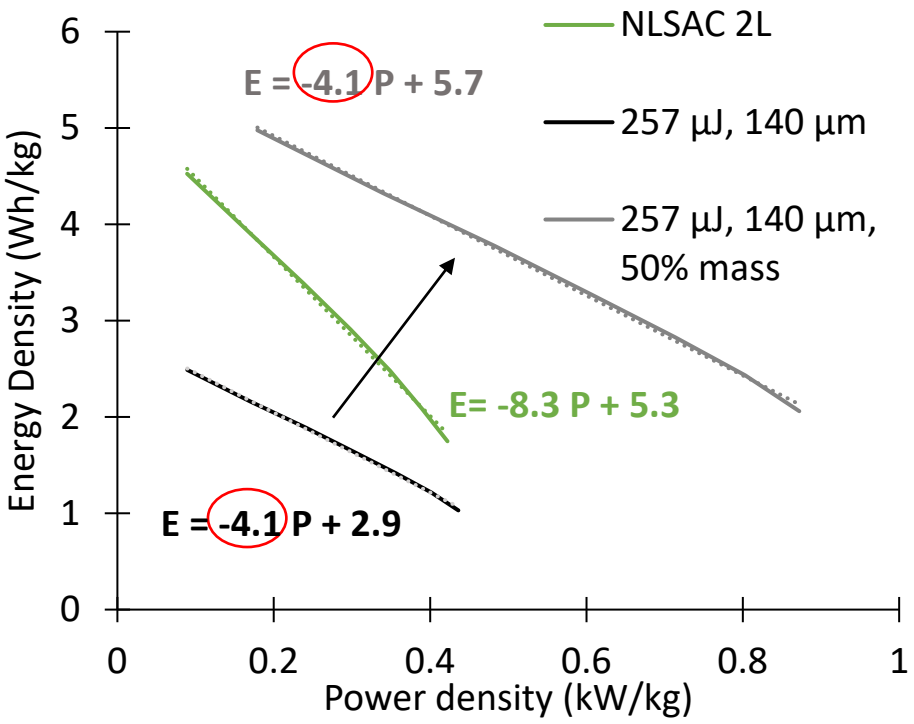

$C = \frac{\int i(t)dt}{\int dV}$
$E = \frac{1}{2} C \Delta V^2$
$P = \frac{E}{\Delta t}$
ΔV
Δt
Potential (V)
0.5
0.3
0.1
-0.1
-0.3
-0.5
0
30
60
90
120
150
180
210
240
270
Time (s)

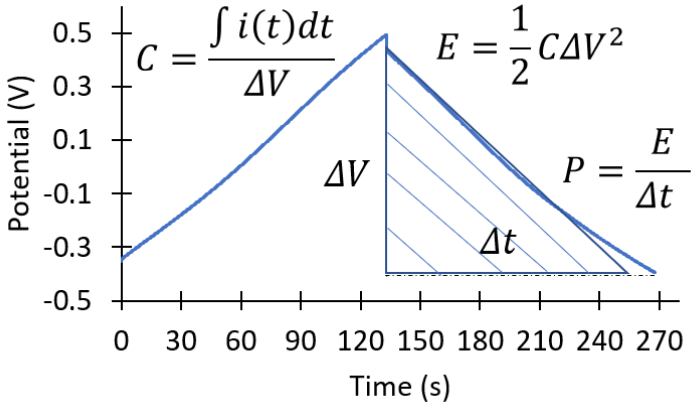
Results


NLSAC 2L
257 µJ, 140 µm
E= -8.3 P + 5.3
E = -4.1 P + 2.9
Energy Density (Wh/kg)
Power density (kW/kg)
0
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1


$C = \frac{\int i(t)dt}{\int dV}$
$E = \frac{1}{2}C\Delta V^2$
$P = \frac{E}{\Delta t}$
ΔV
Δt
Potential (V)
Time (s)
0.5
0.3
0.1
-0.1
-0.3
-0.5
0
30
60
90
120
150
180
210
240
270

Results

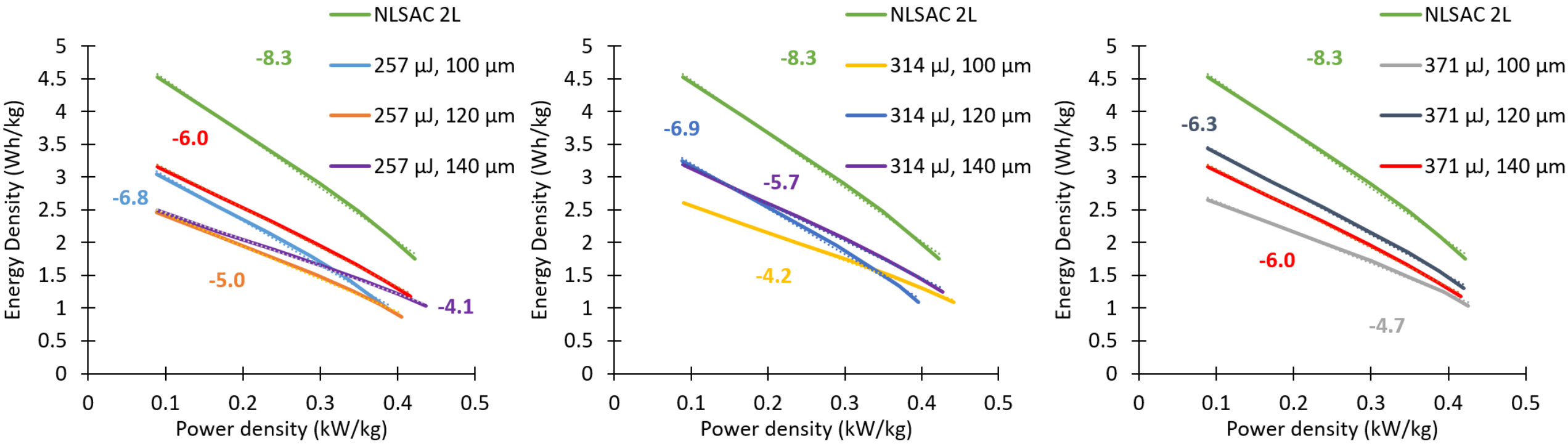




The mass of the electrodes changes the absolute values of the energy and power densities, but not the slope of the Ragone plot!

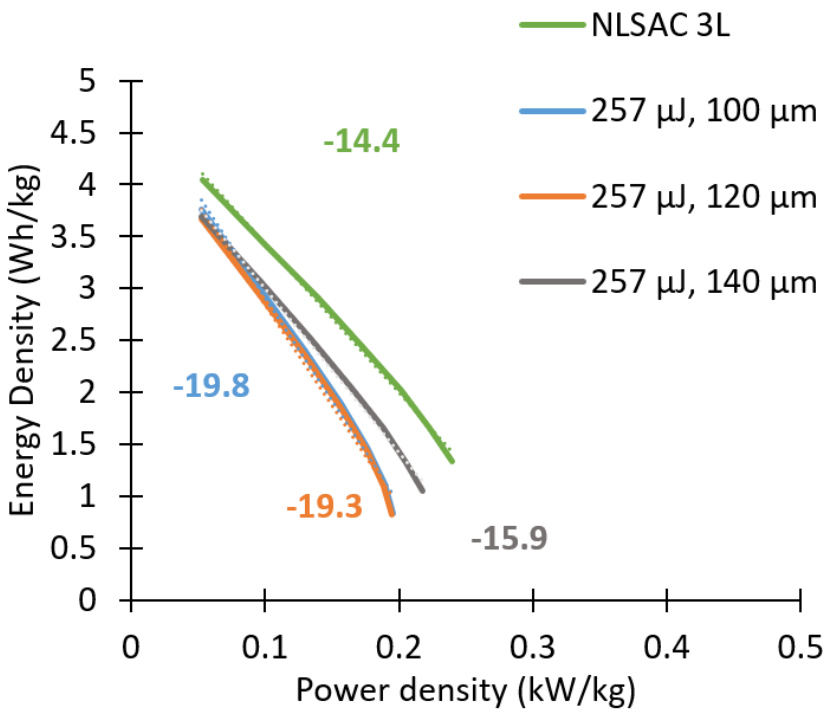
Results

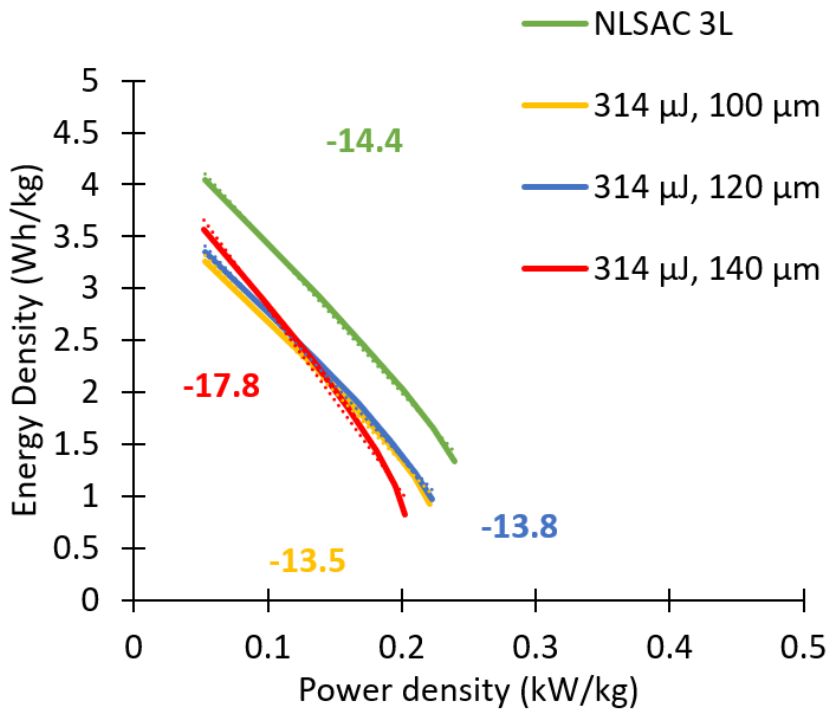
2 Layers

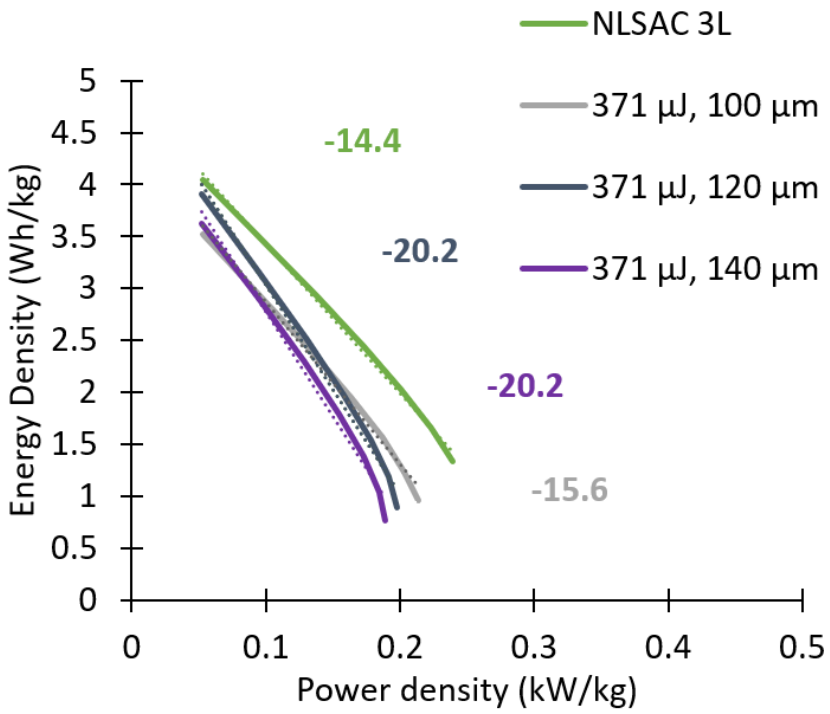


Results

3 Layers

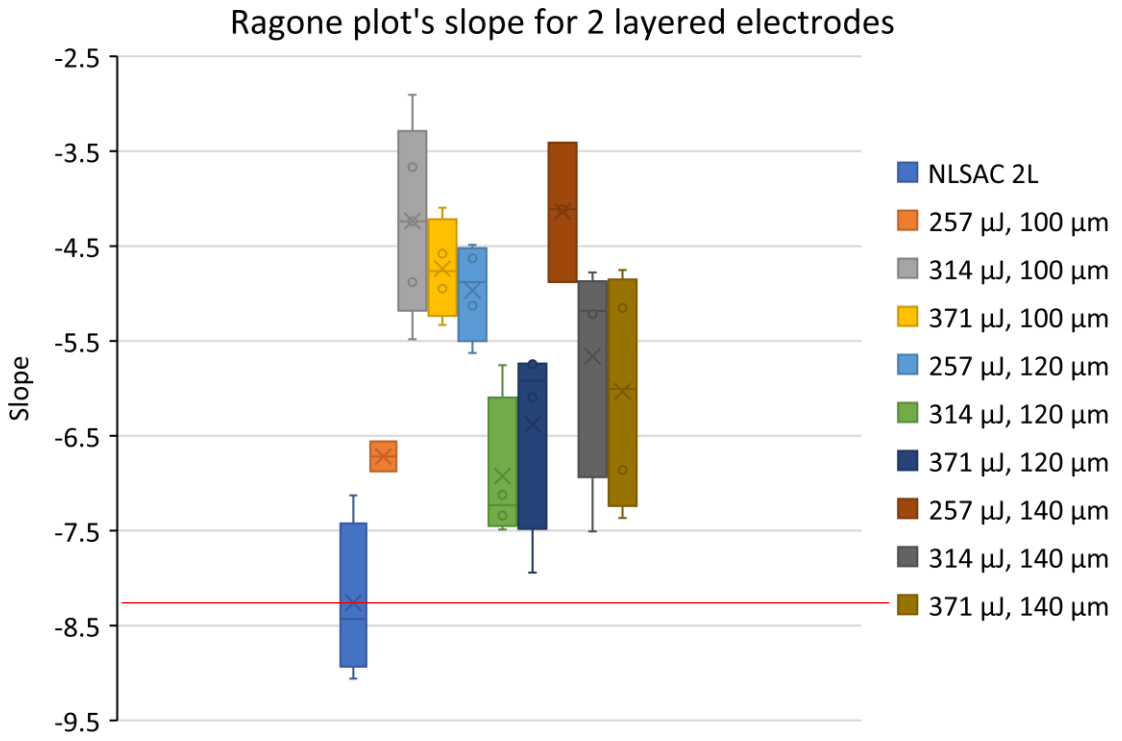






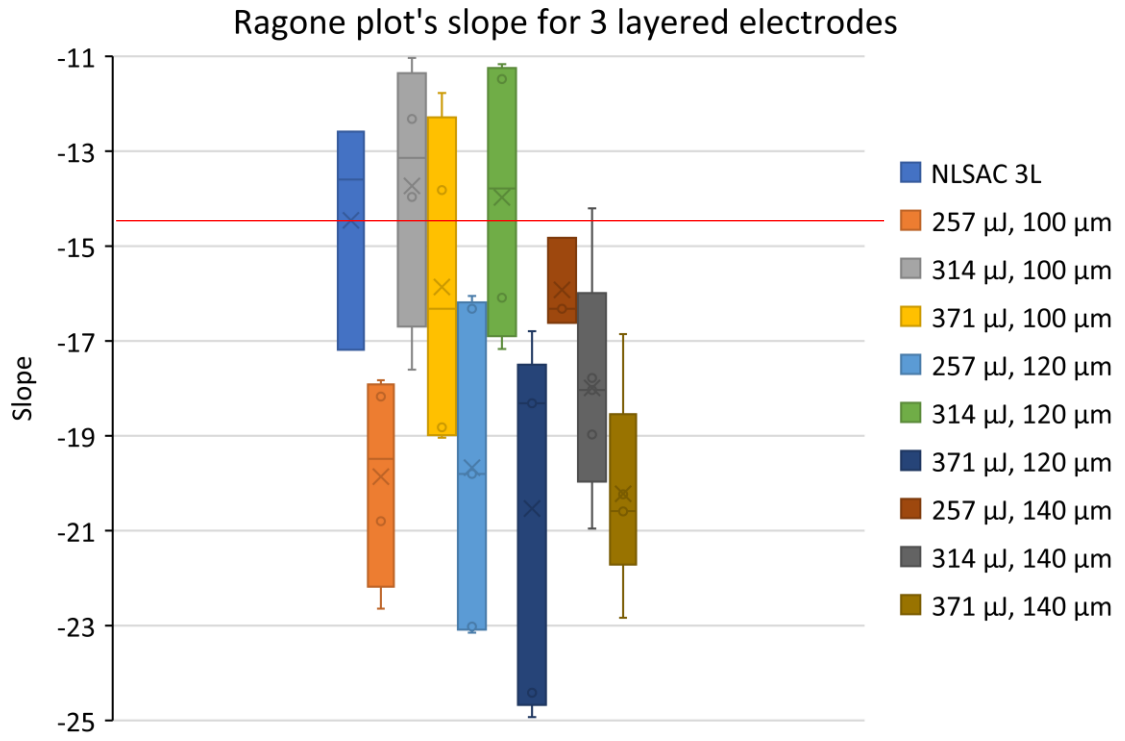
Results

All laser-processed electrodes had a smaller slope than the references



	257 µJ	314 µJ	371 µJ
100 µm	-6.8	-4.2	-4.7
120 µm	-5.0	-6.9	-6.3
140 µm	-4.1	-5.7	-6.0

The slopes of the laser-processed electrodes are either similar or larger than the references



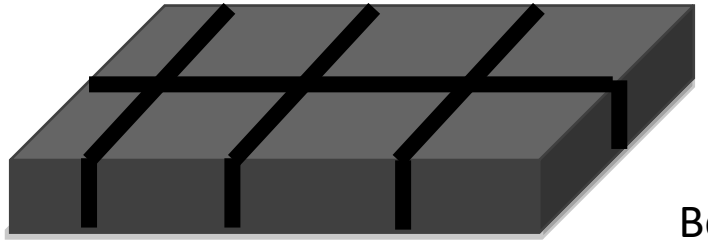
	257 µJ	314 µJ	371 µJ
100 µm	-19.8	-13.5	-15.6
120 µm	-19.3	-13.8	-20.2
140 µm	-15.9	-17.8	-20.2

Discussion and Future Work

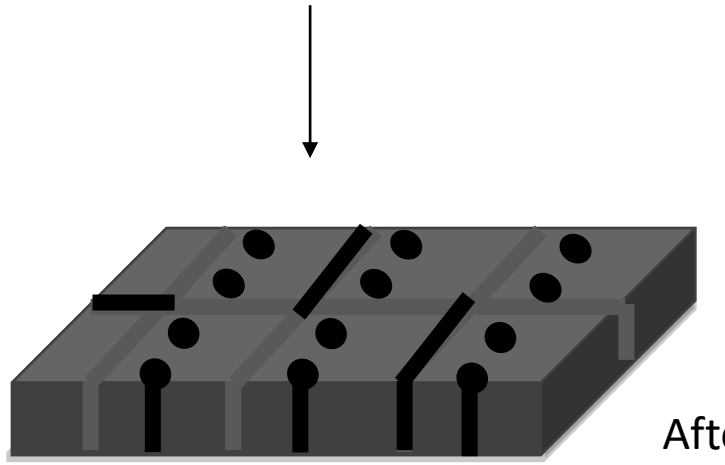
- The assessment of the actual energy and power densities of laser-processed electrodes depends on the correct quantification of their masses
- The effect of the laser-scribing on the electrochemical performance was partially masked by the pattern induced by screen-printing
- All the 2-layered laser-scribed electrodes had a smaller Ragone plot's slope than the non-laser scribed ones, suggesting that ionic diffusion had been improved at high rates
- For these electrodes, the most promising laser-scribing condition seems to be 140 µm at 257 µJ and the least favourable, 120 µm at 314 µJ
- For the 3-layered electrodes, the slopes of the laser-processed electrodes are either similar or even larger than those of the non-laser processed ones

Discussion and Future Work

2 layers

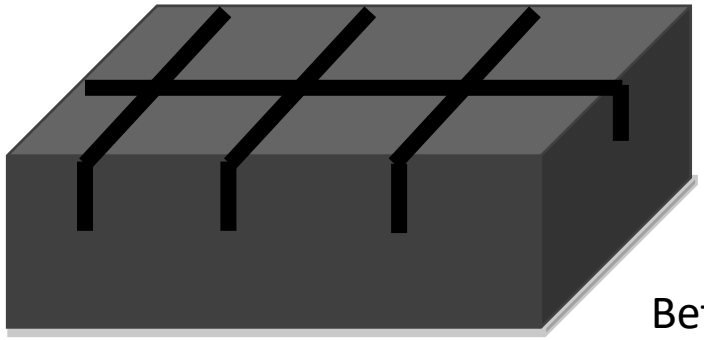


Before laser scribing?

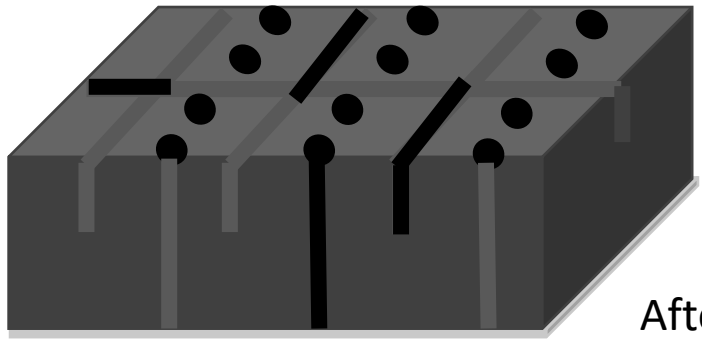


After laser scribing?

3 layers



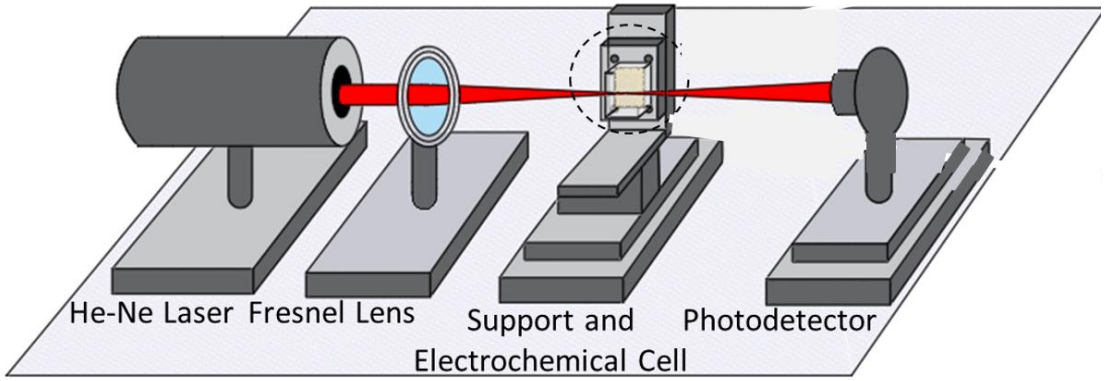
Before laser scribing?

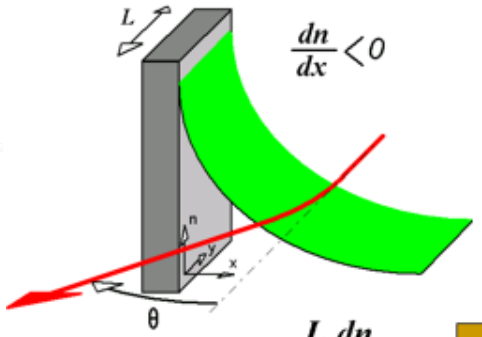


After laser scribing?

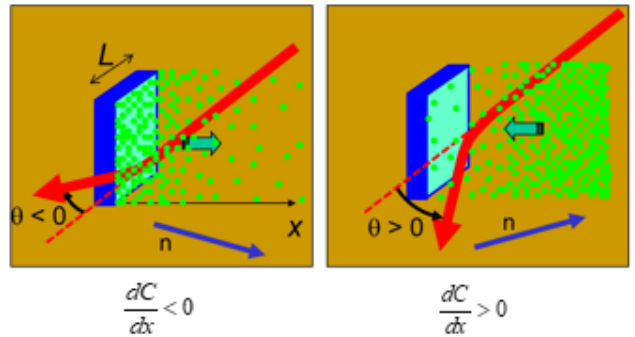
Discussion and Future Work

After solving the previous issues, Probe Beam Deflection (PBD) will be used to study the ionic diffusion within the laser--processed electrodes:





$$\theta = \frac{L}{n}\frac{dn}{dx}$$



J. Baptista, IDL & Loughborough University (**jpbaptista@fc.ul.pt**)

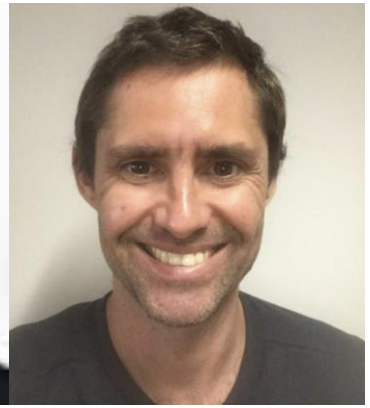
Dr. G. Gaspar, IDL

D. Santos, IDL & CQE

A. Guerra, IDL

Professor J. Correia, CQE

Professor U. Wijayantha, Loughborough University



Professor K. Lobato, IDL

The authors declare no conflict of interests

Thank you! ☺

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