Why High-precision coulombic tracking and lithium plating studies require thermal baths?*

Alana Zülke

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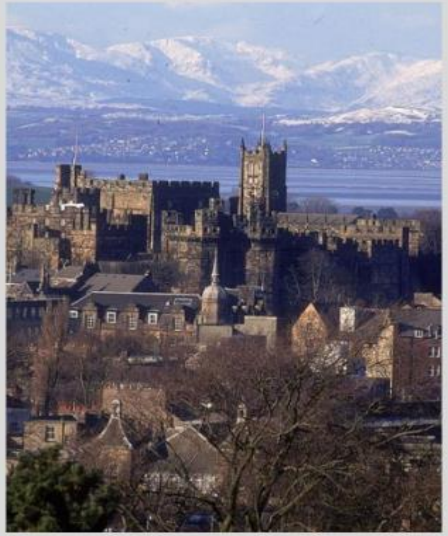

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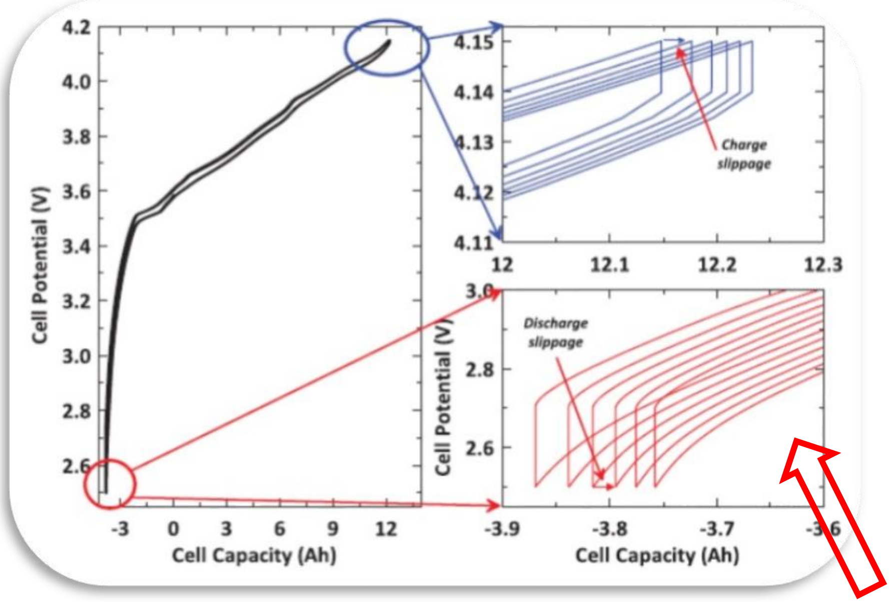
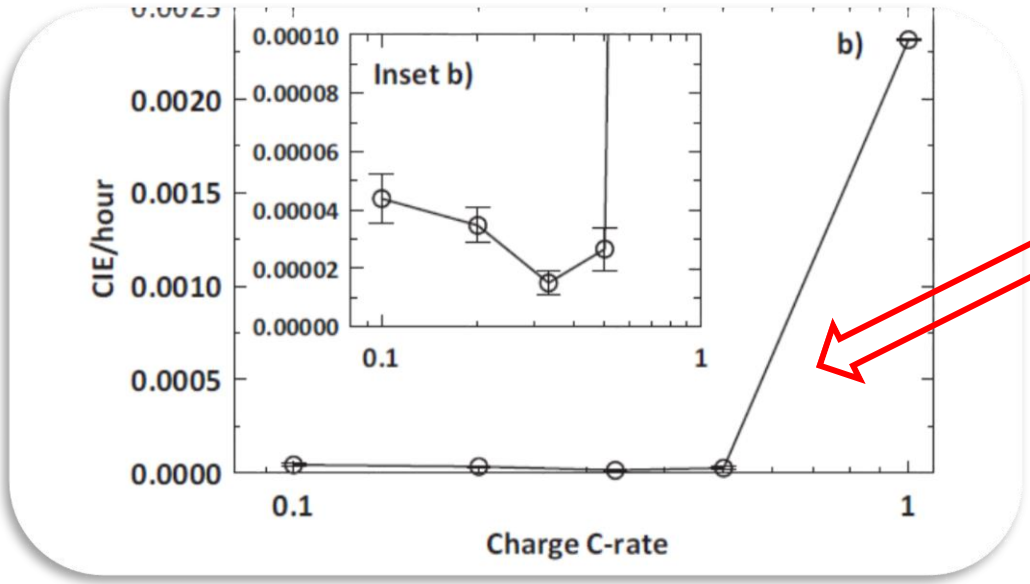
HIGH PRECISION COULOMETRY (HPC) : advantages and *pitfalls*





Flag Lithium Plating

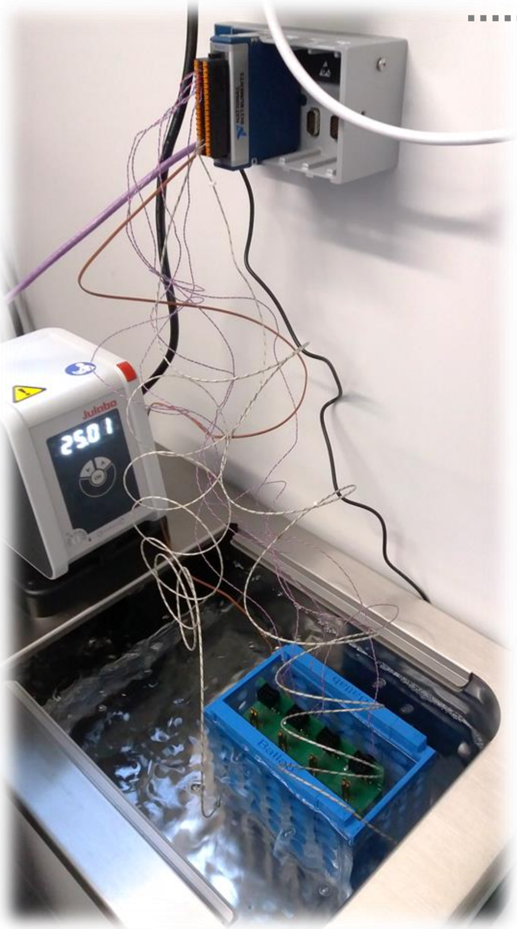
There is **no** HPC if ΔT > 1K

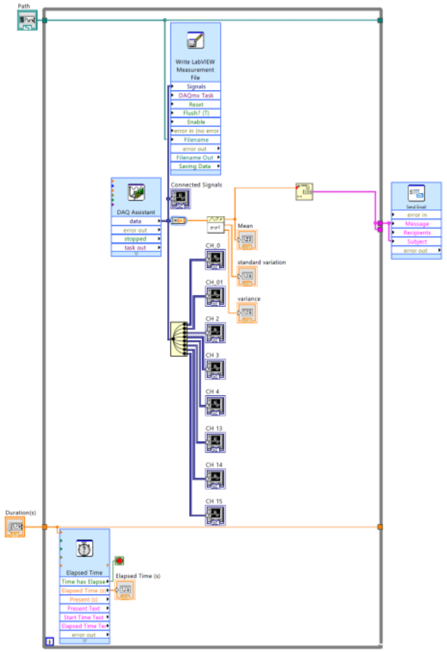
Table I. Factors that affect the ability to precisely and accurately measure CE. For the purpose of these estimates, dQ/dV has been assumed to be the full cell capacity in 1 V and dV/dT has been assumed to be 100 μV/K. ΔQ is the percentage error in the cell capacity, ΔI is the percentage accuracy in the current, ΔV is the precision of the voltage measurement, Δt is the interval between voltage measurements, and ΔT is the precision of the temperature control.

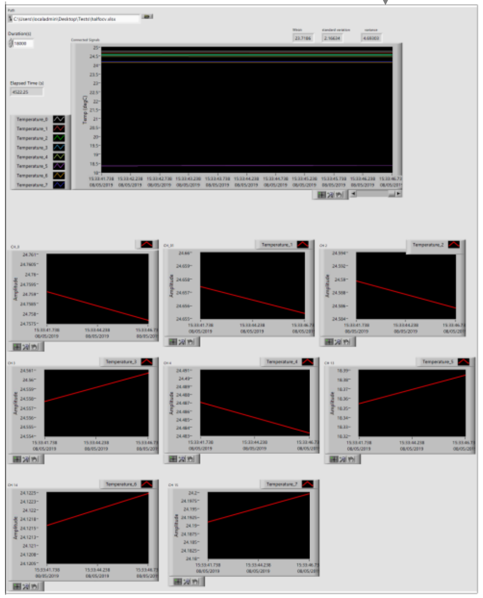
Parameter	Associated error	Desired error in Q (%)	For C/10 rate measurements	For C-rate measurement
ΔI	$\Delta Q = \Delta I t$	<0.01	$\Delta I < 0.01\%$	$\Delta I < 0.01\%$
ΔV	$\Delta Q = dQ/dV\ \Delta V$	<0.01	$\Delta V < 0.0001$ V	$\Delta V < 0.0001$ V
Δt	$\Delta Q = I\Delta t$	<0.01	$\Delta t < 3.6$ s	$\Delta t < 0.36$ s
ΔT	$\Delta Q = dV/dT\ dQ/dV\ \Delta T$	<0.01	$\Delta T < 1$ K	$\Delta T < 1$ K

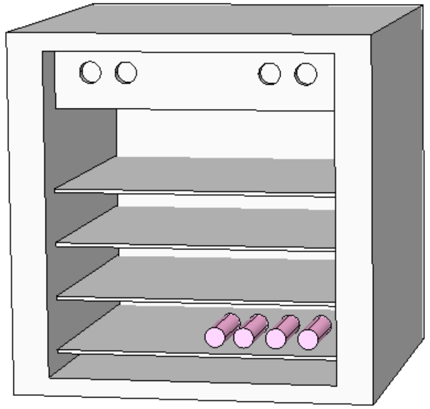
Simulated and calculated temperature profiles upon a series of cycling tests, including fast charging - modifying only the thermal boundary conditions

16 TC/module



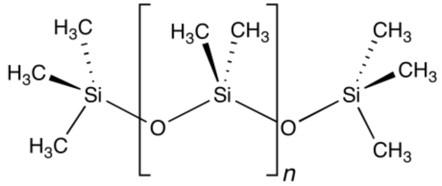


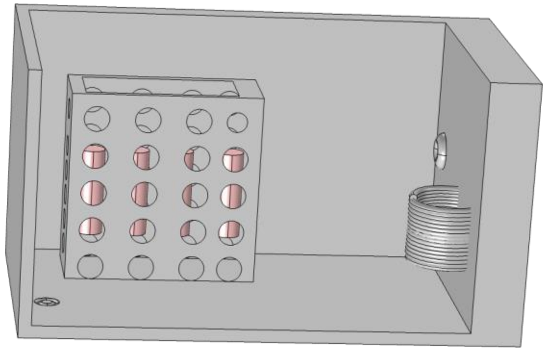




Integrated thermal chamber of the HPC tester

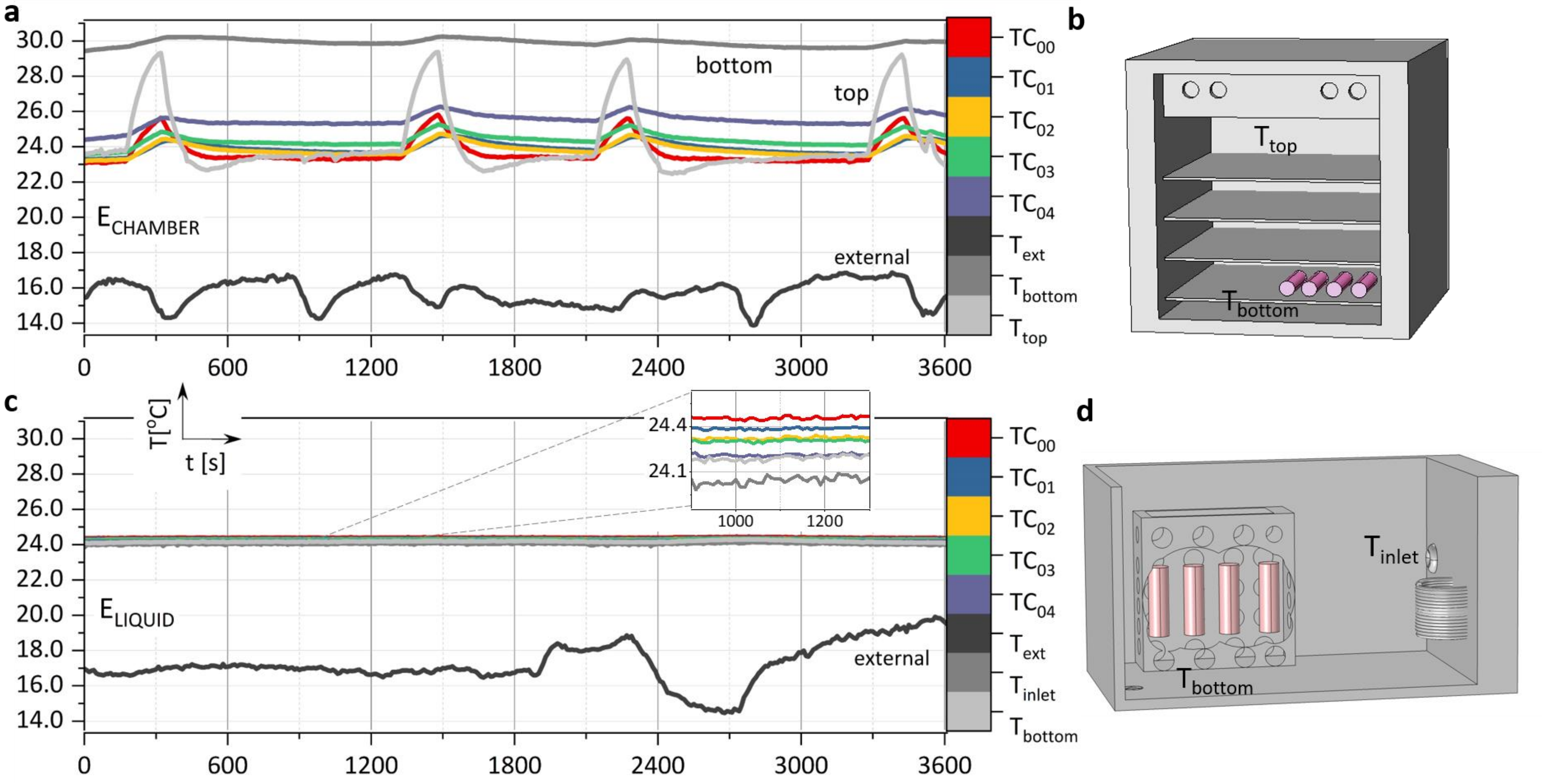
NCA|graphite 3.4Ah





PMDS-filled thermal bath poly(dimethylsiloxane)

Most chamber designs are not ideal for HPC (…)



Spatial-temp fluctuations
$\Delta T > 5K$

Limit HPC and DTV

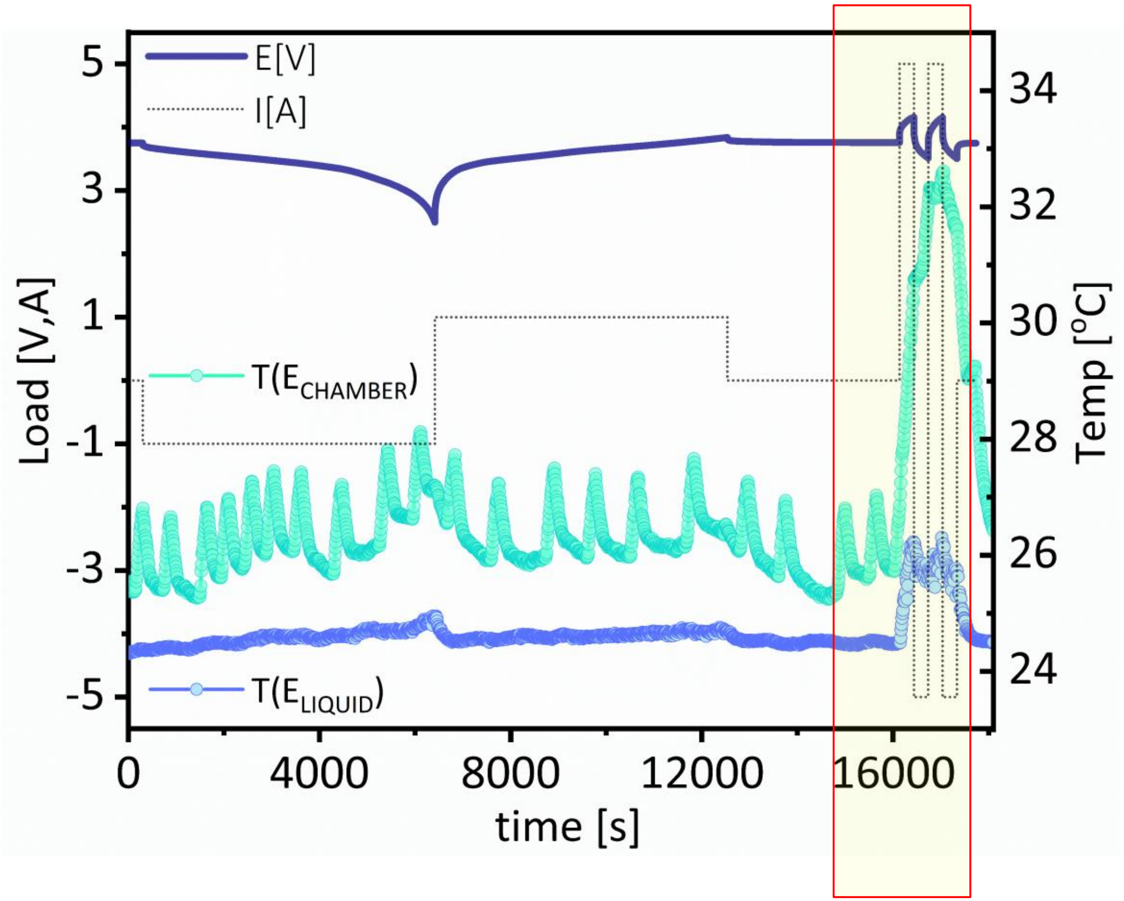
Eliminate eventual TEMP fluctuations
$\Delta T > 1K$

Eliminate spatial TEMP gradients

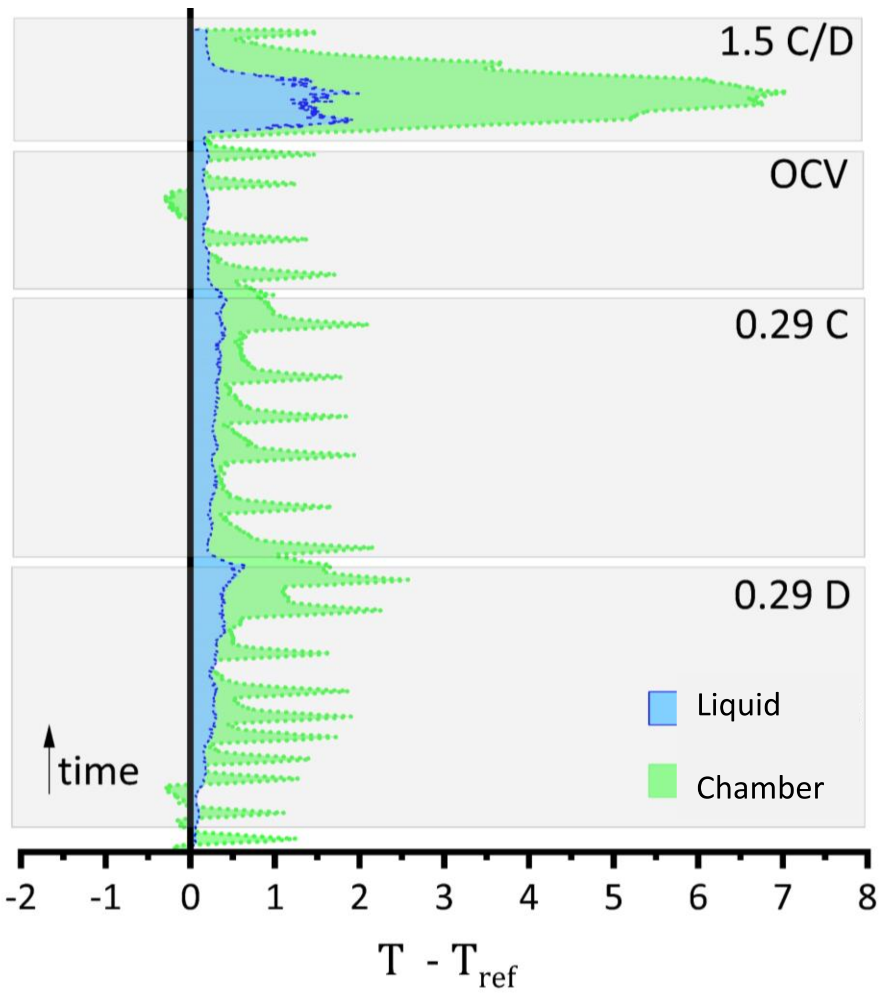
HPC and DTV enabled

Thermal Profiles during cycling

a



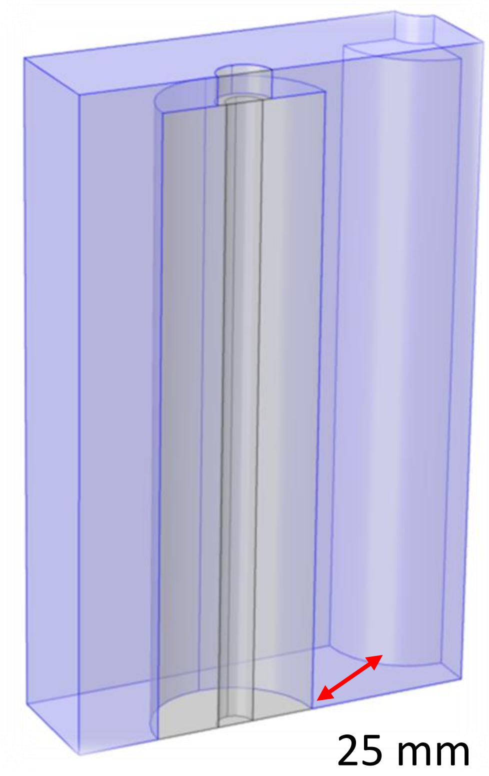
b

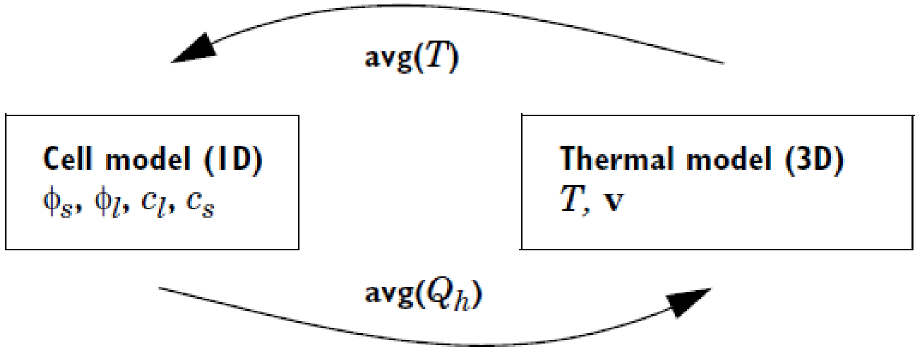


Liquid → $\Delta T > 0$ at C/3

FEA using COMSOL Multiphysics (existing lithium-ion battery model / pre-built interface)
Packages: Electrochemistry, Batteries and Fuel Cells, Heat transfer in Solid and Fluids, Laminar Flow.

System: Cylindrical Cell (Graphite|NCA) is placed in a matrix in a battery pack, with a controllable distance between the battery units. A 3D-thermal model is coupled to a 1D-battery model that is used to generate a heat source in the active battery material. The resulting temperature profile is the balance between the heat generated and dissipated.





$$Avg\ (Q_h)$$

$$q_r = \frac{\int_0^{l_n+l_s+l_p} j^{Li}(\Phi_s - \Phi_e - U)dx}{l}$$

$$q_e = \frac{\int_0^{l_n+l_s+l_p} j^{Li} T \frac{\partial U}{\partial T} dx}{l}$$

$$q_j = \frac{\int_0^{l_n+l_s+l_p} \left[\sigma^{eff}\left(\frac{\partial \Phi_s}{\partial x}\right)^2 + k^{eff}\left(\frac{\partial \Phi_e}{\partial x}\right)^2 + \frac{2k^{eff}RT}{F}\left(1 - t_+^0\right)\frac{\partial(\ln c_e)}{\partial x}\frac{\partial \Phi_e}{\partial x}\right]dx}{l}$$

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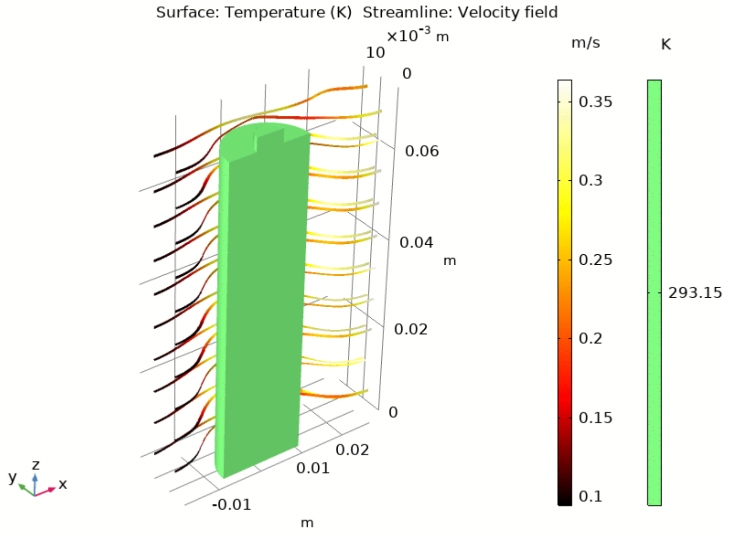
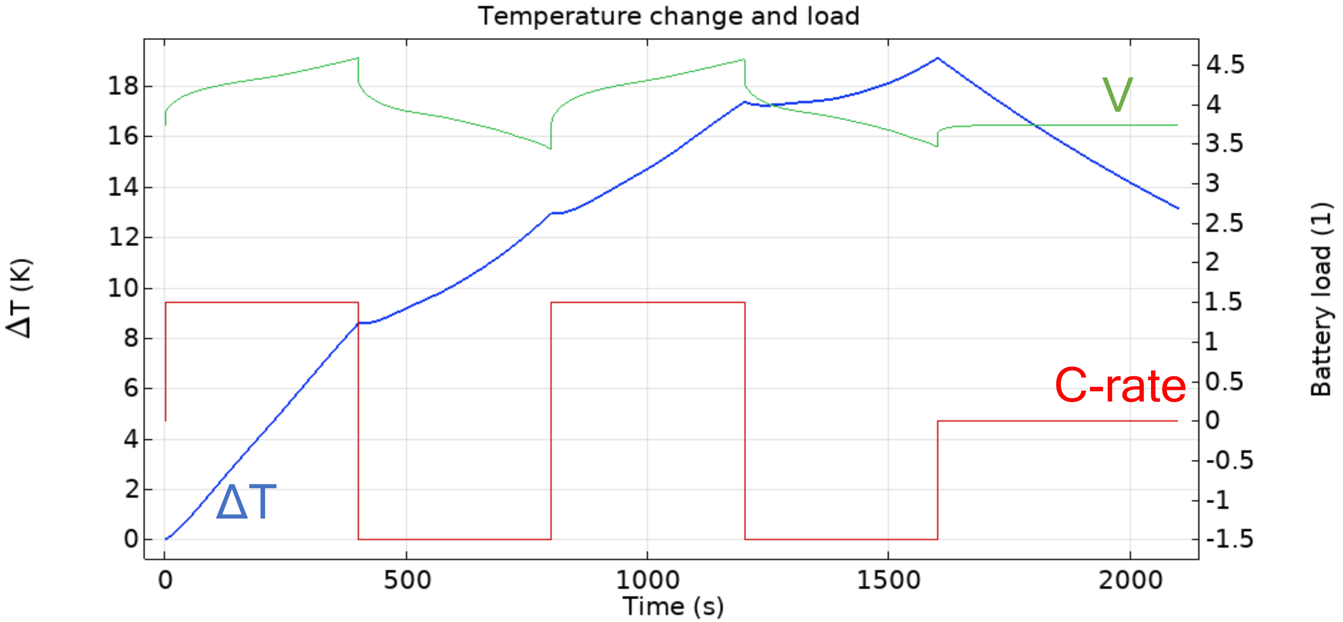
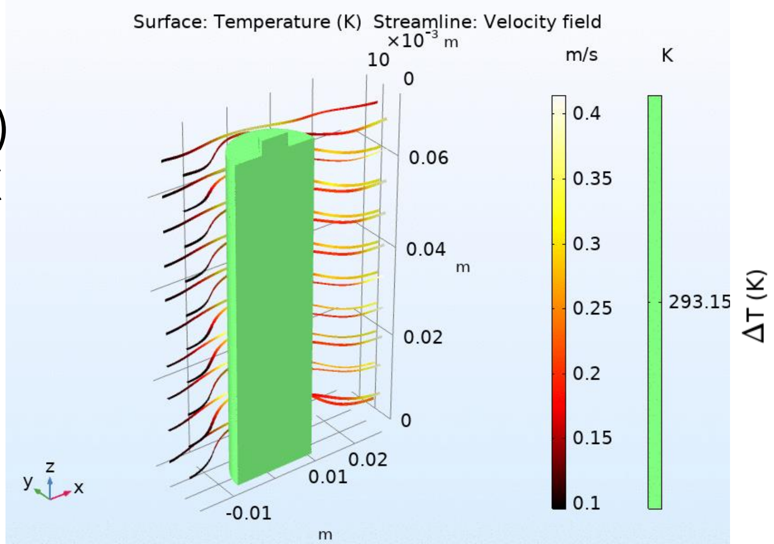
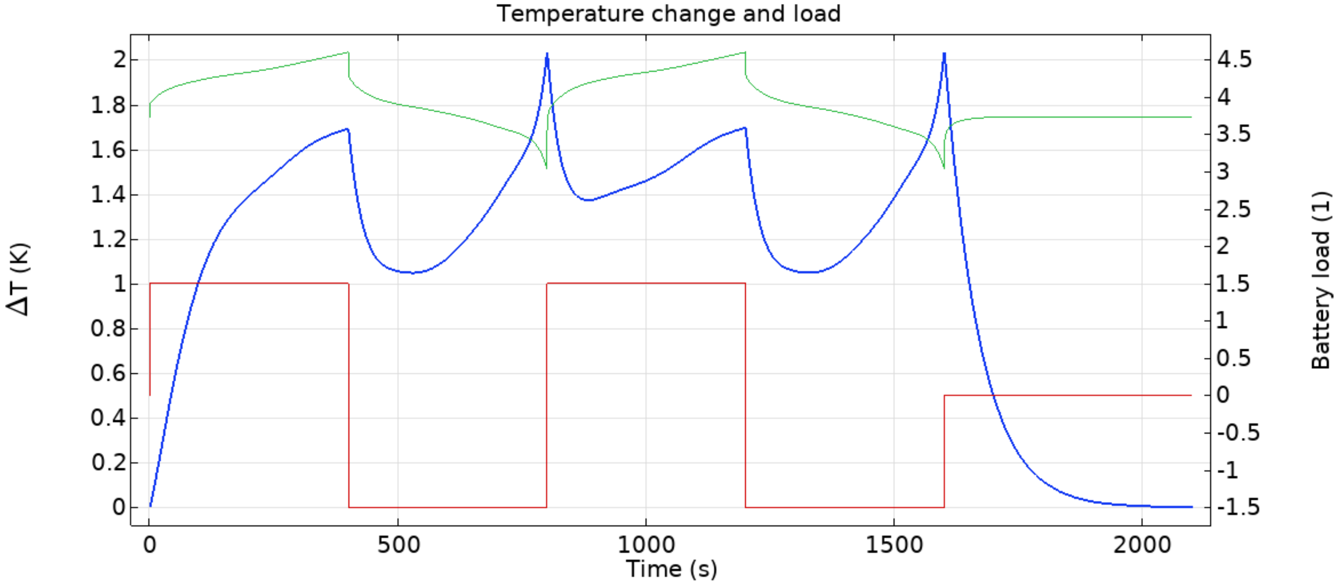
AIR
Tref = 291.15

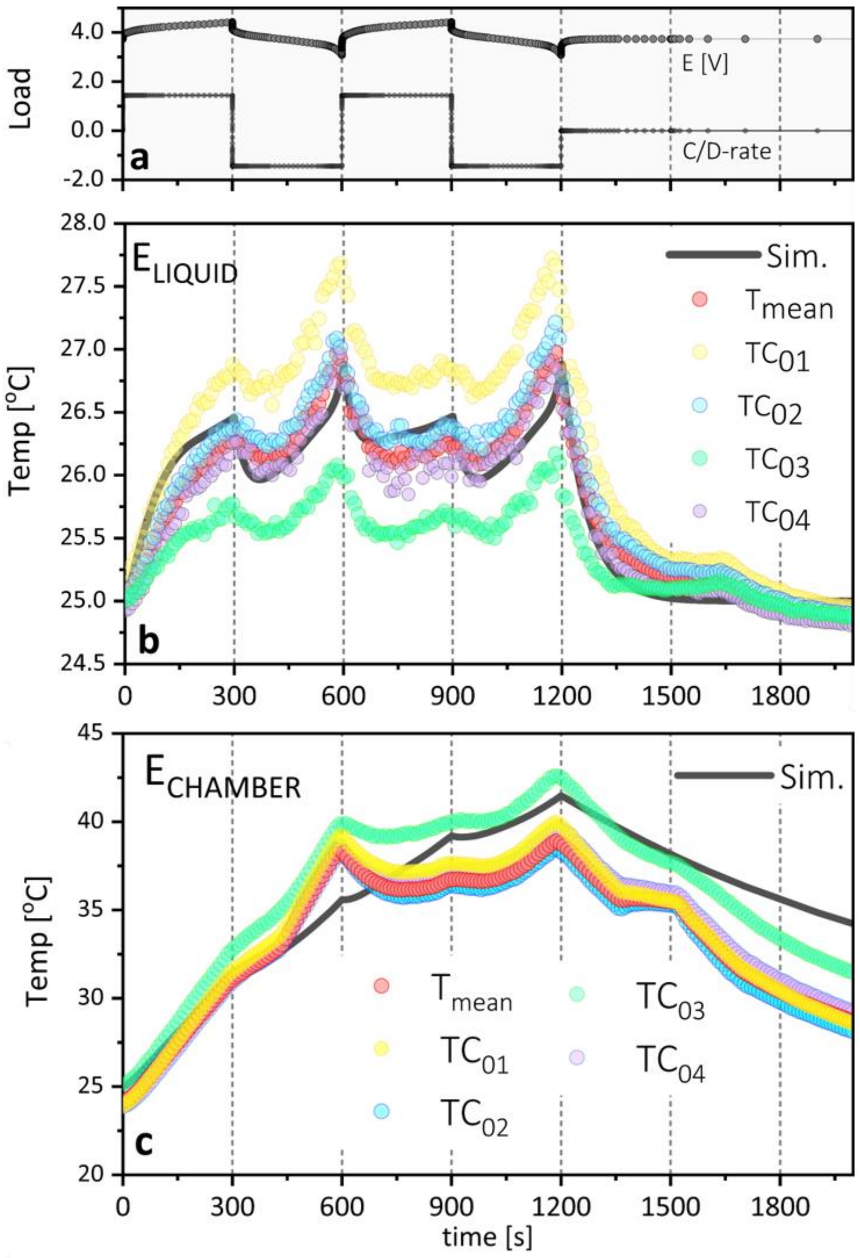




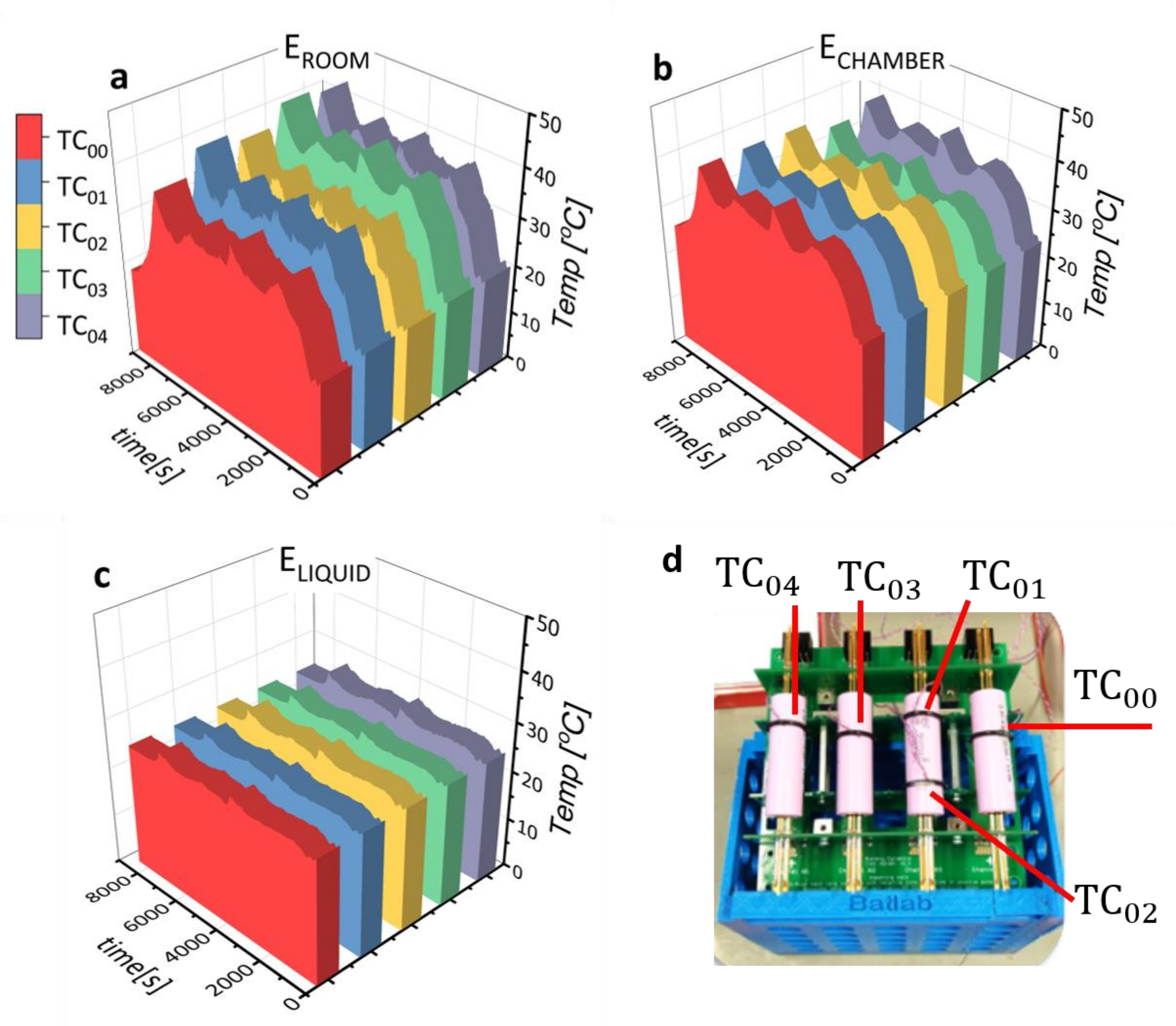
LIQUID (PDMS)
Tref = 298.15 K



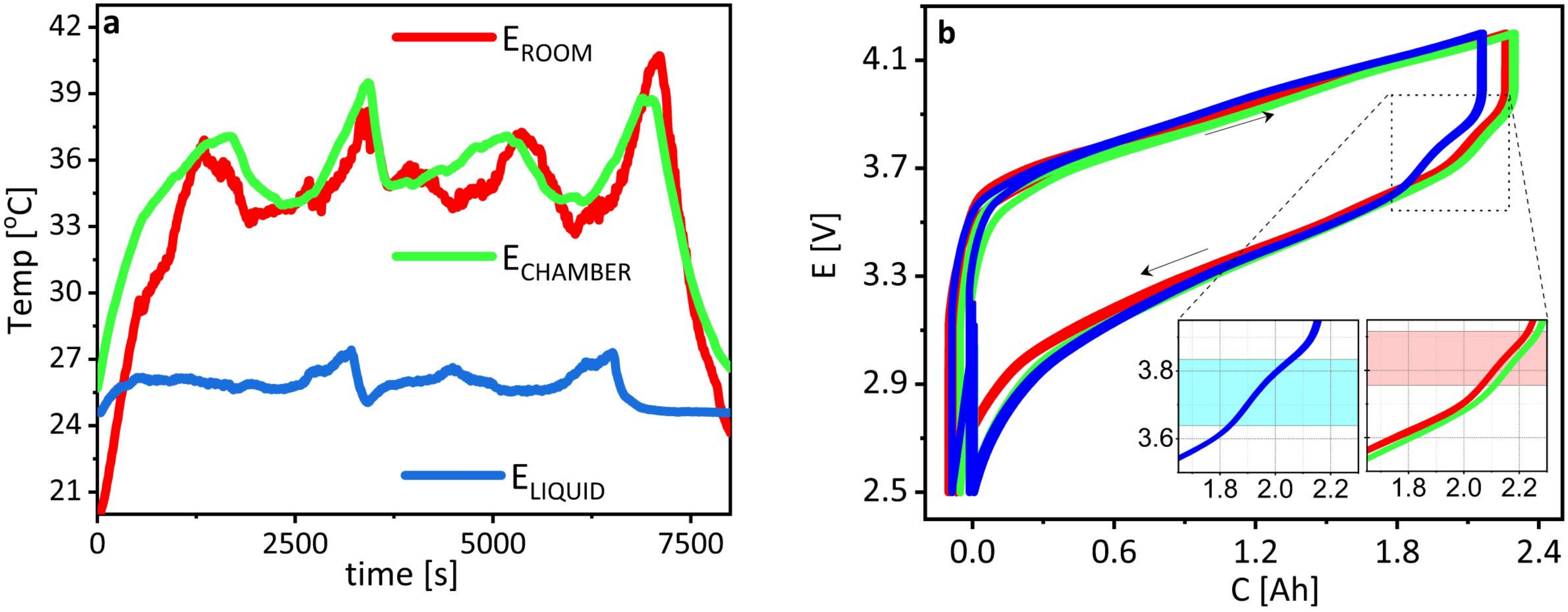




Simulated (Sim) and experimental temperature profiles of NCA cylindrical batteries when cycled in direct contact with PDMS (b) and inside the tester‘s thermal chamber (c). Duty cycle shown in (a). TC00-04 are surface-mounted thermocouples on 4 different batteries and Tmean represents the average value.



Typical temperature profile detected at the NCA batteries upon two consecutive 5 A pulses when conditioned in (a) the thermal chamber of the tester, at (b) room temperature and (c) in the PDMS-filled thermal bath. Location of the sensors is indicated by (d).



Mean temperature at the cell surface of NCA cylindrical batteries upon 1.5 C/D-rate cycles in different conditioning environments. Mean temperature profiles (a) voltage-capacity curves (b).

SUMMARY

- Poor cell temperature control limits HPC and DTV. Many thermal chambers are not proper for these studies.
- To be meaningful, the required condition of $\Delta T < 1K$ can be achieved by **direct-contact cooling**
- **Fast charging and lithium plating studies call for direct-contact cooling with dielectric fluids in baths.** Li plating can be severely underestimated as a result of untracked temperature variations at the cell level.

A final IMPORTANT alert…

AMAZONAS HAS DECLARED EMERGENCY STATE

Thank you very much!

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Tuesday , 3rd

Yi Li – Parallel Session 2a | 4 pm

Wed, 4th - Parallel Session 5a | 4pm
Michael Mercer

Beatrice Wolff

Robert Burrell

Shahin Nikman

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Thu, 5th - Parallel Session 6b
Denes Csala

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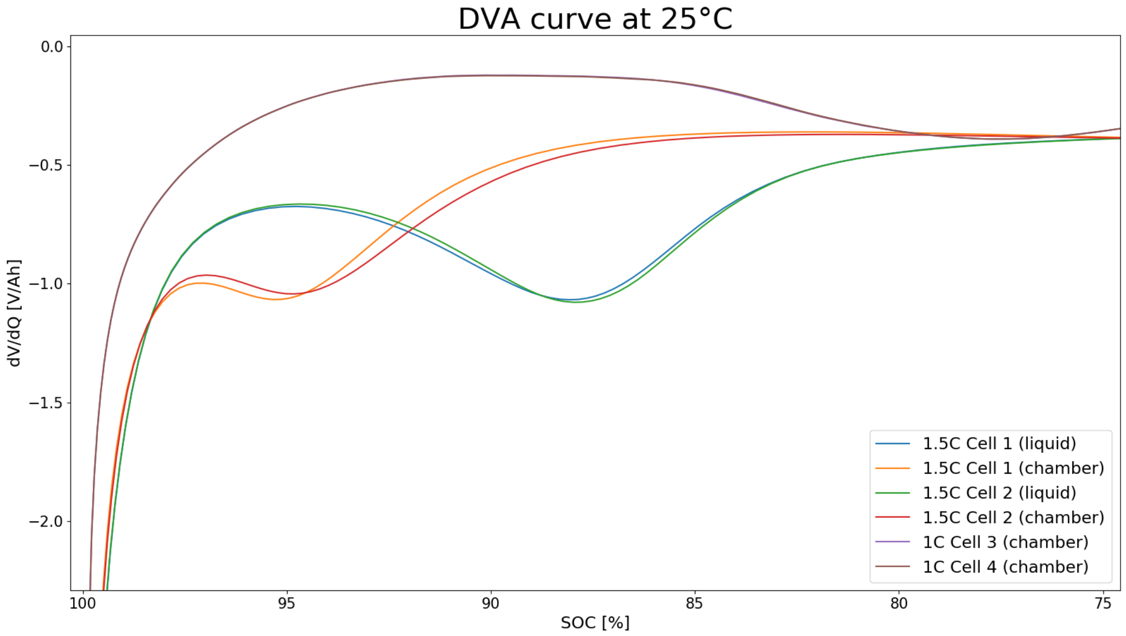
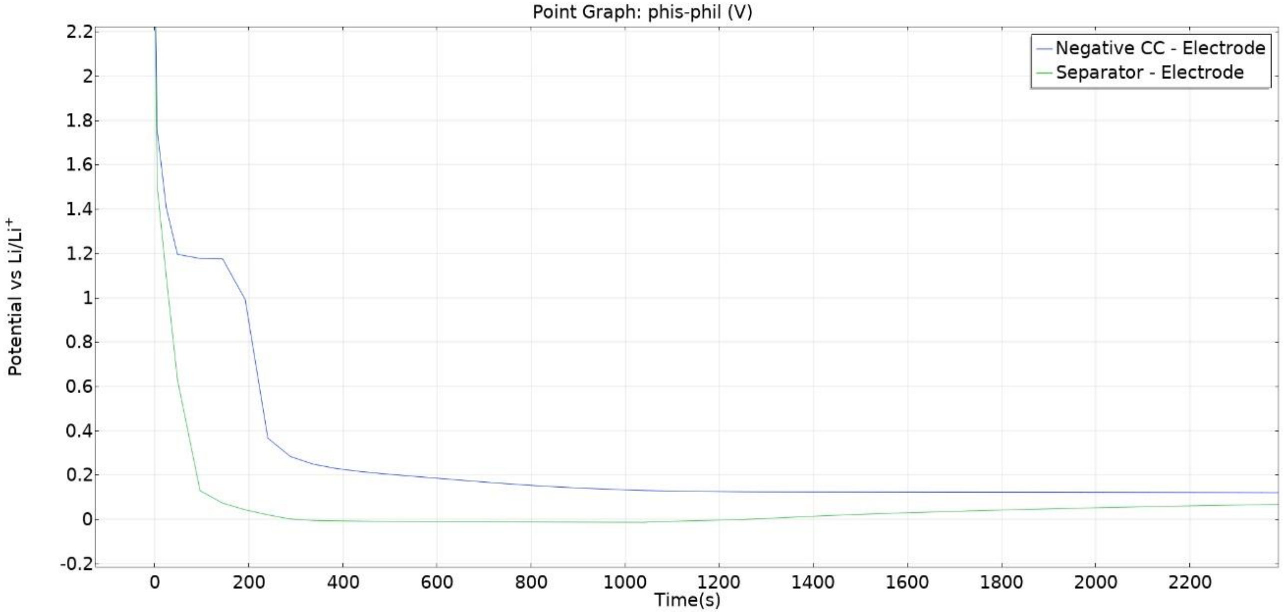
Lithium Plating Indication



Estimated overpotential visited by the negative electrode at the interface with current collector and separator. This calculation estimated the local overpotential at the (-)electrode|separator to reach -0.014V.



ELECTROCHEMICAL MODEL – GOVERNING EQUATIONS

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2}\nabla \cdot \left(r^2 \nabla c_s\right)$$ ***[diffusion of lithium in solid electrode particles]***

$$a_s F j_n = \nabla \cdot \left(\sigma^{\text{eff}} \nabla \phi_s\right)$$ ***[charge balance in particles; electron current]***

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \nabla \cdot \left(D_e^{\text{eff}} \nabla c_e\right) + a_s(1 - t_+^0) j_n$$ ***[diffusion of lithium in electrolyte]***

$$a_s F j_n = -\nabla \cdot \left(\kappa^{\text{eff}} \left(\nabla \phi_e - \frac{2RT}{F}(1 - t_+^0)\left(1 + \frac{d \ln f_\pm}{d \ln c_e}\right) \nabla \ln c_e\right)\right)$$ ***[ion current]***

$$j_n = k_0 \left(c_{s,e}\right)^{\alpha_c} \left(c_{s,\text{max}} - c_{s,e}\right)^{\alpha_a} \left(c_e\right)^{\alpha_a} \left(\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp\left(-\frac{\alpha_a F}{RT}\eta\right)\right)$$ ***[reaction rate]***

$$\eta = \phi_s - \phi_e - U_{\text{ocp}}(c_{s,e}) - j_n F R_{\text{film}}$$

PDEs of P2D Model		Boundary Conditions	
Charge conservation in electrolyte phase (domain = +, –, sep)			
$\frac{\partial \Phi_e(x,t)}{\partial x} = -\frac{i_e(x,t)}{\kappa} + \frac{2R_g T(x,t) t_a^0}{F} \frac{\partial \ln c_e(x,t)}{\partial x}$	(1)	$\kappa^{\pm} \frac{\partial \Phi_e}{\partial x}\Big\vert_{x=0^{\pm}} = 0, \quad \kappa^{+} \frac{\partial \Phi_e}{\partial x}\Big\vert_{x=L^{+}} = \kappa^{sep} \frac{\partial \Phi_e}{\partial x}\Big\vert_{x=0^{sep}}, \quad \kappa^{sep} \frac{\partial \Phi_e}{\partial x}\Big\vert_{x=L^{sep}} = \kappa^{-} \frac{\partial \Phi_e}{\partial x}\Big\vert_{x=L^{-}}$	
$\frac{\partial i_e(x,t)}{\partial x} = aFj(x,t) = \frac{3\varepsilon_s}{R_p} Fj(x,t) = J(x,t)$	(2)	$i_e(x,t)\vert_{x=0^{\pm}} = 0, \quad i_e(x,t)\vert_{x=L^{\pm}} = i_e(x,t)\vert_{x\in[0^{sep},L^{sep}]} = i_{app}(t)\ ,\ j(x,t)\vert_{x\in[0^{sep},L^{sep}]} = 0$	
Charge conservation in solid phase (domain = +, –)			
$\frac{\partial \Phi_s(x,t)}{\partial x} = -\frac{i_s(x,t)}{\sigma}$	(3)	$\sigma^{\pm} \frac{\partial \Phi_s}{\partial x}\Big\vert_{x=0^{\pm}} = -i_{app}(t), \quad \sigma^{+} \frac{\partial \Phi_s}{\partial x}\Big\vert_{x=L^{+}} = \sigma^{sep} \frac{\partial \Phi_s}{\partial x}\Big\vert_{x=0^{sep}}, \quad \sigma^{sep} \frac{\partial \Phi_s}{\partial x}\Big\vert_{x=L^{sep}} = \sigma^{-} \frac{\partial \Phi_s}{\partial x}\Big\vert_{x=L^{-}}$	
$\frac{\partial i_s(x,t)}{\partial x} = -aFj(x,t) = -\frac{3\varepsilon_s}{R_p} Fj(x,t) = -J(x,t)$	(4)	$i_s(x,t)\vert_{x=0^{\pm}} = i_{app}(t), \quad i_s(x,t)\vert_{x=L^{\pm}} = i_s(x,t)\vert_{x\in[0^{sep},L^{sep}]} = 0$	
Mass conservation in electrolyte phase (domain = +, –, sep)			
$\frac{\partial c_e(x,t)}{\partial t} = \frac{1}{\varepsilon_e} \frac{\partial}{\partial x}\left(D_e \frac{\partial c_e(x,t)}{\partial x}\right) + \frac{t_a^0}{F\varepsilon_e} \frac{\partial i_e(x,t)}{\partial x}$	(5)	$\frac{\partial c_e}{\partial x}\Big\vert_{x=0^{\pm}} = 0, \ D_e^{+} \frac{\partial c_e}{\partial x}\Big\vert_{x=L^{+}} = D_e^{sep} \frac{\partial c_e}{\partial x}\Big\vert_{x=0^{sep}}, \ D_e^{sep} \frac{\partial c_e}{\partial x}\Big\vert_{x=L^{sep}} = D_e^{-} \frac{\partial c_e}{\partial x}\Big\vert_{x=L^{-}}$	
Mass conservation in solid phase (domain = +, –)			
$\frac{\partial c_s(x,r,t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial c_s(x,r,t)}{\partial r}\right)$	(6)	$\frac{\partial c_s}{\partial r}\Big\vert_{r=0^{\pm}} = 0, \quad D_s^{\pm} \frac{\partial c_s}{\partial r}\Big\vert_{r=R_p^{\pm}} = -j(x,t), \quad c_s\vert_{r=R_p^{+}} = c_{ss}^{+}(x,t), \quad c_s\vert_{r=R_p^{-}} = c_{ss}^{-}(x,t)$	
AEs of P2D model (domain = +, –)			
$j(x,t) = \frac{2i_0(x,t)}{F} \sinh\left(\frac{F\eta_s(x,t)}{2R_g T(x,t)}\right)$	(7)	$i_0(x,t) = Fk_0 \sqrt{c_e(x,t)(1 - c_{ss}(x,t))c_{ss}(x,t)}$	(8)
$\eta_s(x,t) = \Phi_s(x,t) - \Phi_e(x,t) - U_{ss} - r_f(x,t) J(x,t) / a$	(9)	$U_{ss}(\theta_{ss},T) = U_{ss}^{*} + \frac{\partial U_{ss}}{\partial T}\Big\vert_{T^{*}} (T(x,t) - T^{*}) = f_s(\theta_{ss}) + f_T(\theta_{ss})(T(x,t) - T^{*})$	(10)
Output equation of P2D model			
$V_{bat}(t) = \Phi_s(0^{+},t) - \Phi_s(0^{-},t) + (r_{col}^{+} + r_{col}^{-}) i_{app}(t)$	(11)		

- The equations and the boundary conditions that describe the heat transfer phenomenon in the Li-ion cell is given as[5]

$$\rho c_p \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(\lambda \frac{\partial T(x,t)}{\partial x}\right) + q_T(x,t)$$

$$q_T(x,t) = q_{T,\mathrm{ohm}}(x,t) + q_{T,\mathrm{rxn}}(x,t) + q_{T,\mathrm{rev}}(x,t)$$

$$\lambda \left.\frac{\partial T(x,t)}{\partial x}\right|_{x=0^+,0^-} = h(T_{\mathrm{end}} - T(x,t))\Big|_{x=0^+,0^-}$$

$$q_{T,\mathrm{ohm}}(x,t) = \sigma\left(\frac{\partial \Phi_e(x,t)}{\partial x}\right)^2 + \kappa \frac{\partial \Phi_e(x,t)}{\partial x}\left(\frac{\partial \Phi_e(x,t)}{\partial x} + \frac{2RT(x,t)t_a^0}{F}\frac{\partial \ln c_e(x,t)}{\partial x}\right)$$

$$q_{T,\mathrm{rxn}}(x,t) = Faj(x,t)\eta_s(x,t)$$

$$q_{T,\mathrm{rev}}(x,t) = Faj(x,t)T(x,t)\left.\frac{\partial U_{\mathrm{ss}}}{\partial T}\right|_{T^*}$$

5. Kumaresan *et al.* *J. Electrochem. Soc.*, **155** (2), A164-A171, 2008