INNOVATIVE SOLUTIONS FOR LITHIUM ION BATTERY FUTURE DEVELOPMENT

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Outline

- A brief introduction to entropymetry
- Applications of entropymetry
- Fast charging methods
  - "Natural charging", Non-linear Volammetry (NLV)
  - "Cascade Pulse Charging" (CPC)
- Summary

A brief introduction to entropymetry

- Basic equations:

$$\Delta G(x) = \Delta H(x) - T\Delta S(x)$$

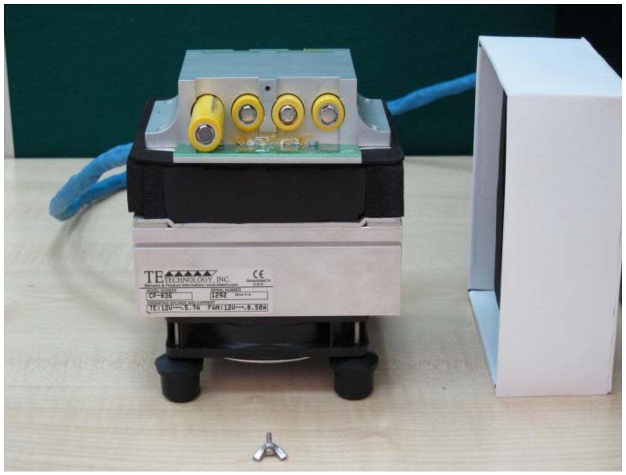
$$\Delta G(x) = -nFE^0(\mathrm{x})$$

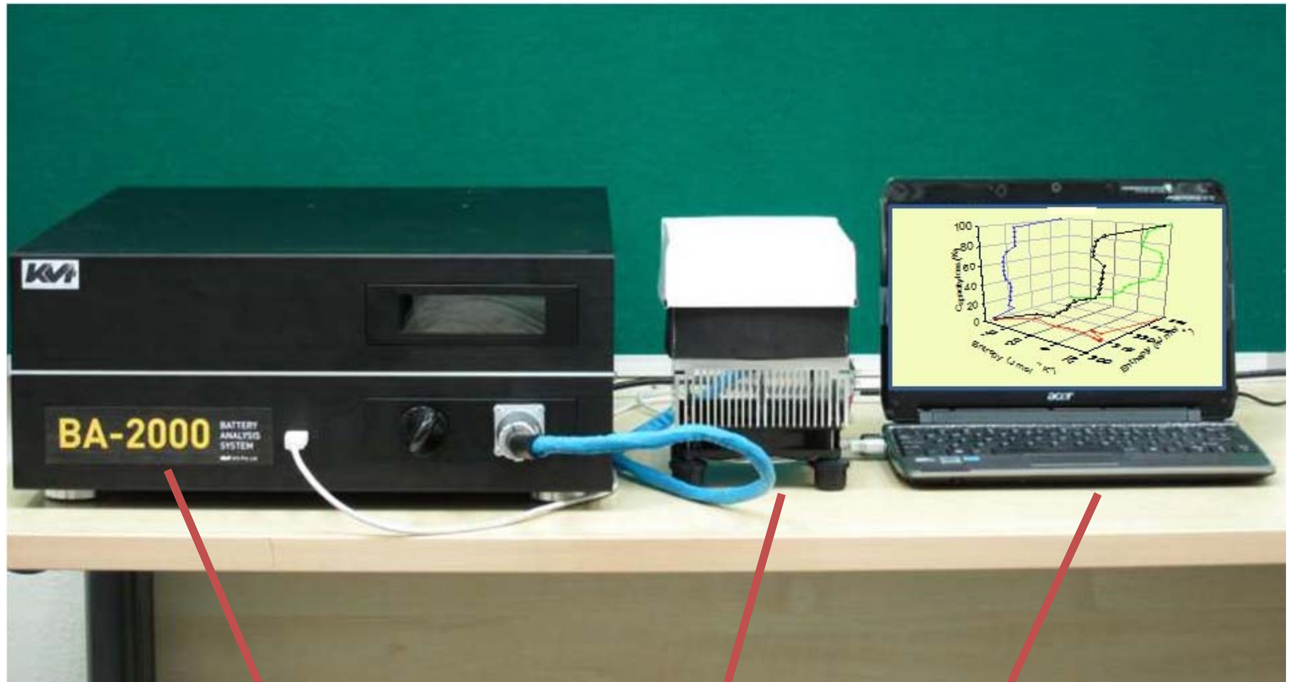
E^0(x)=OCV at any SOC 'x'

$$\Delta S = nF\frac{\partial E^0(x)}{\partial T}$$

$$\Delta H = -nF(E^0 - T\frac{\partial E^0(x)}{\partial T})$$

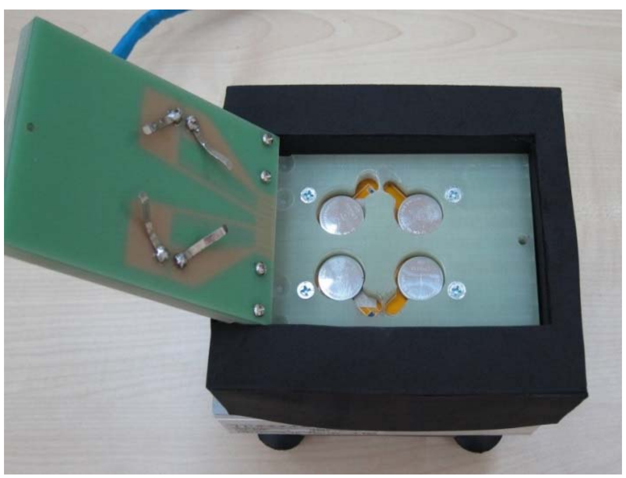
ETMS: BA-2000 Equipment





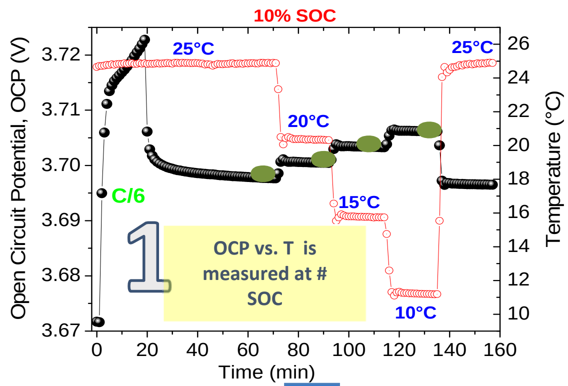
Potentiostat-Galvanostat System

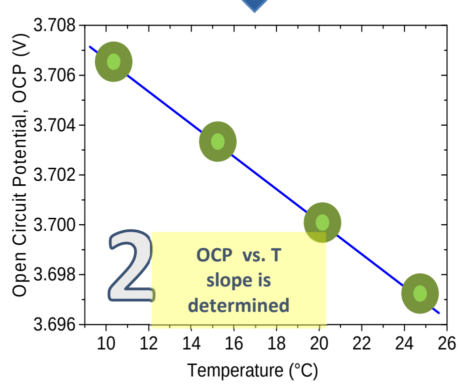
Laptop: Control & Management

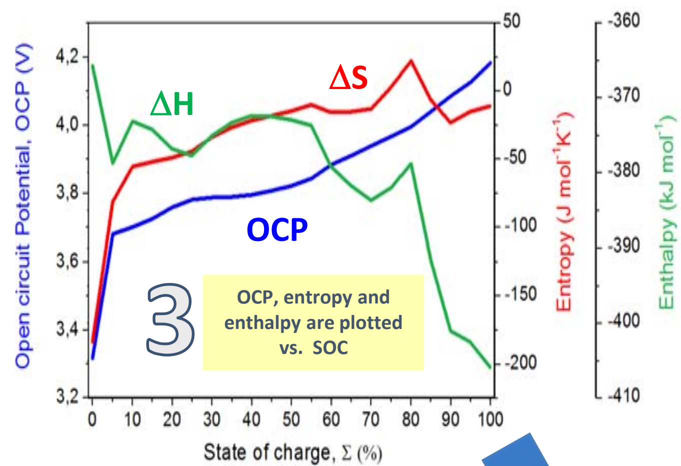


Battery Holder & Temperature Controller

Entropymetry in 3 steps



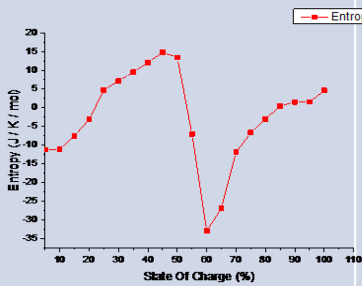
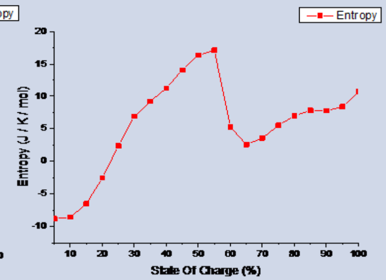
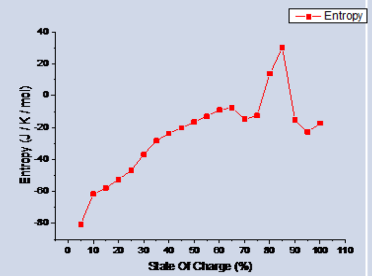
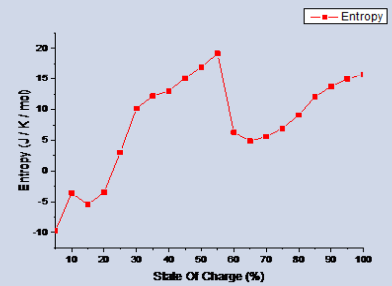




Entropy and enthalpy show more variations than OCP

Applications of entropymetry

1. Chemistry recognition, QC

Cathode composition	NMC $Li_{0.91}Ni_{0.5}Mn_{0.16}Co_{0.35}O_2$	NMC $Li_{0.879}Ni_{0.77}Mn_{0.11}Co_{0.12}O_2$	LCO $Li_{0.9}CoO_2$	NCO $Li_{0.95}Ni_{0.85}Co_{0.15}O_2$
Entropy profile				

2. SOC assessment

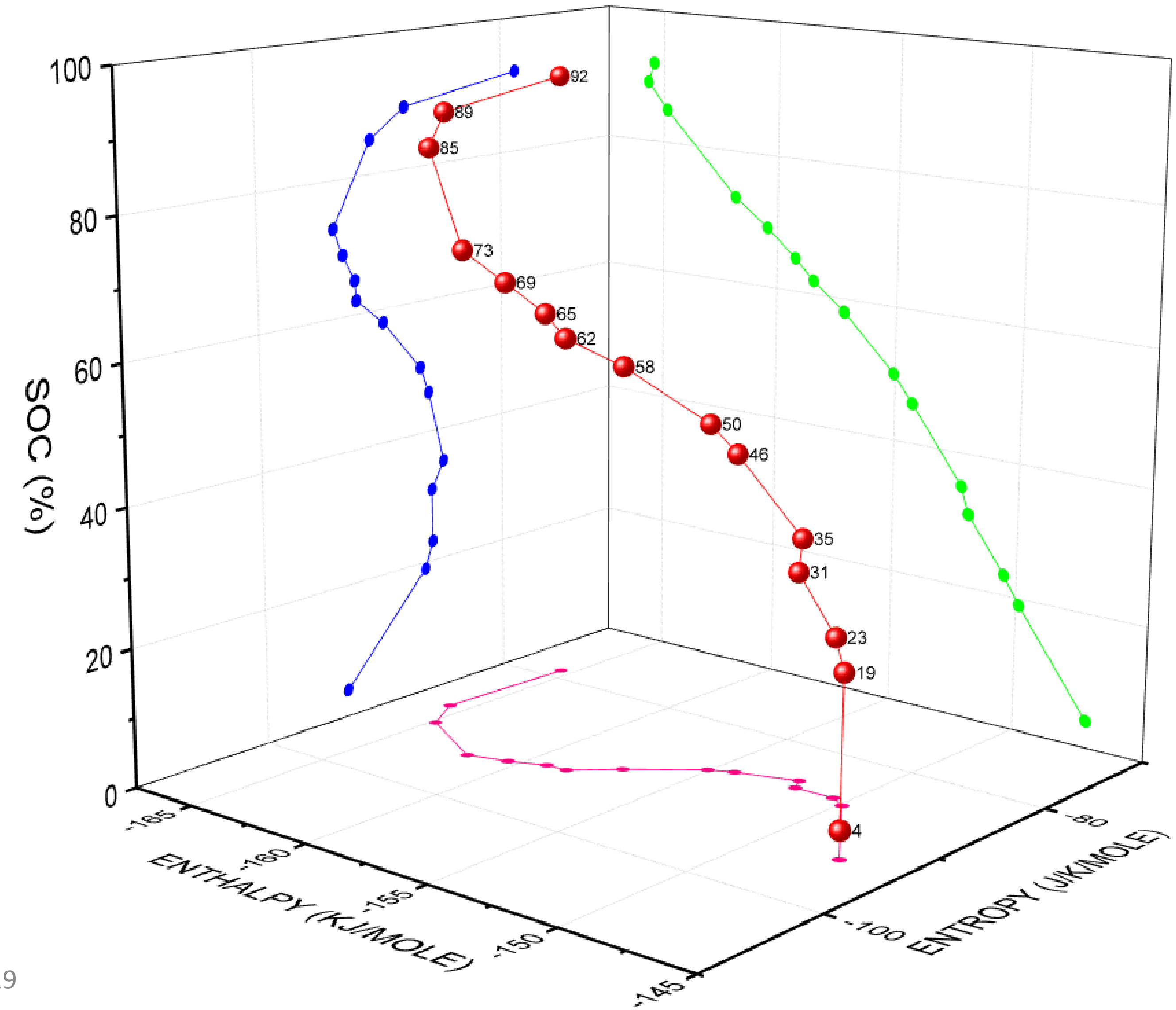
The Universal Battery SOC Law

$$SOC = \alpha + \beta \Delta S + \gamma \Delta H$$

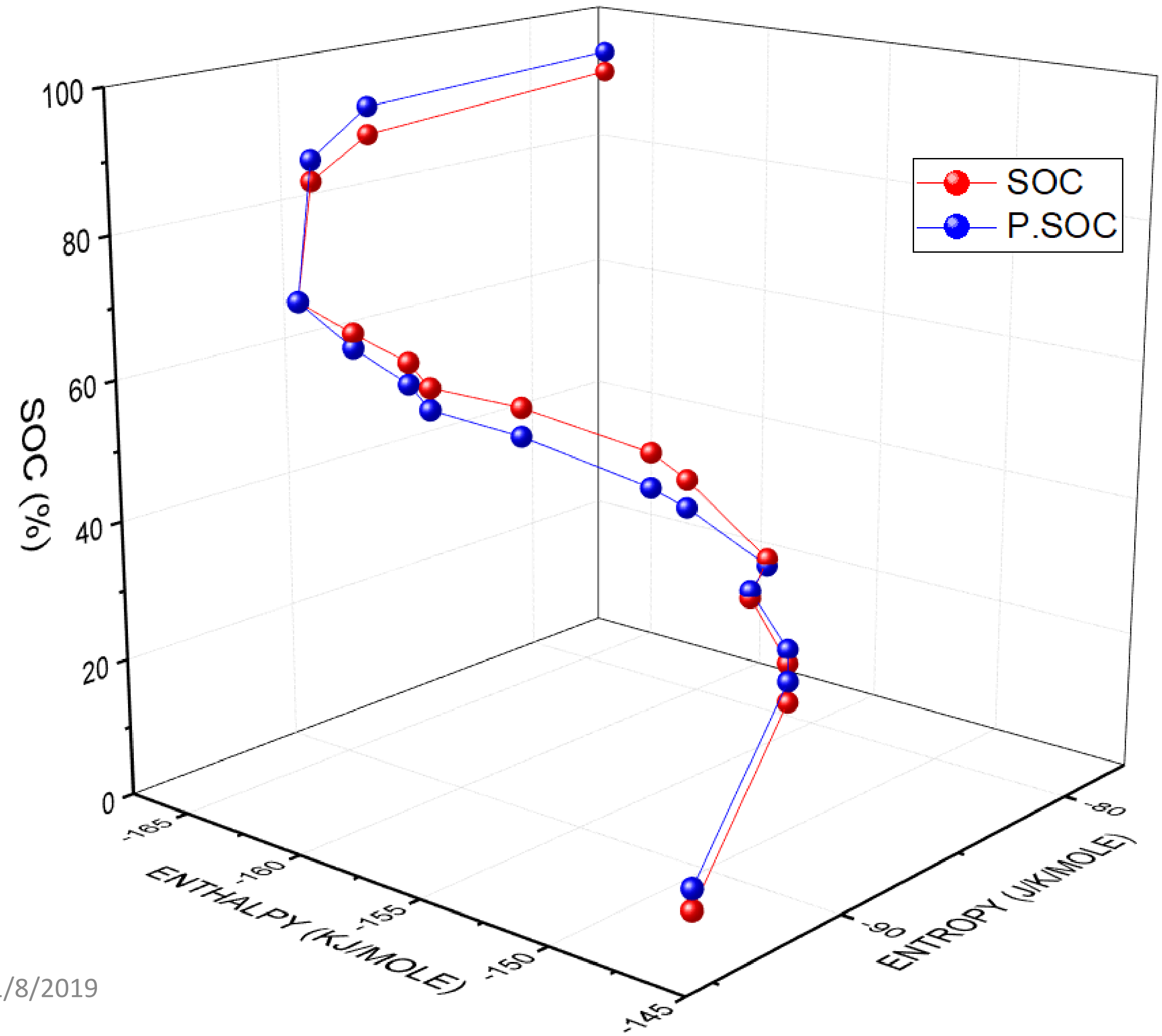
- This law applies to all tested chemistries, including
  - LIB, NiCd, NiMH,
  - Li-MnO_2, Li-FeS_2
  - Alkaline Zn/MnO2 and Zn/C cells
- α, β *and* γ depend on the cell' chemistry and on SOH

1. Alkaline Zn/MnO_2 cells

SOC-ΔS-ΔH 3D plots



SOC simulation



$\alpha = -621.76$

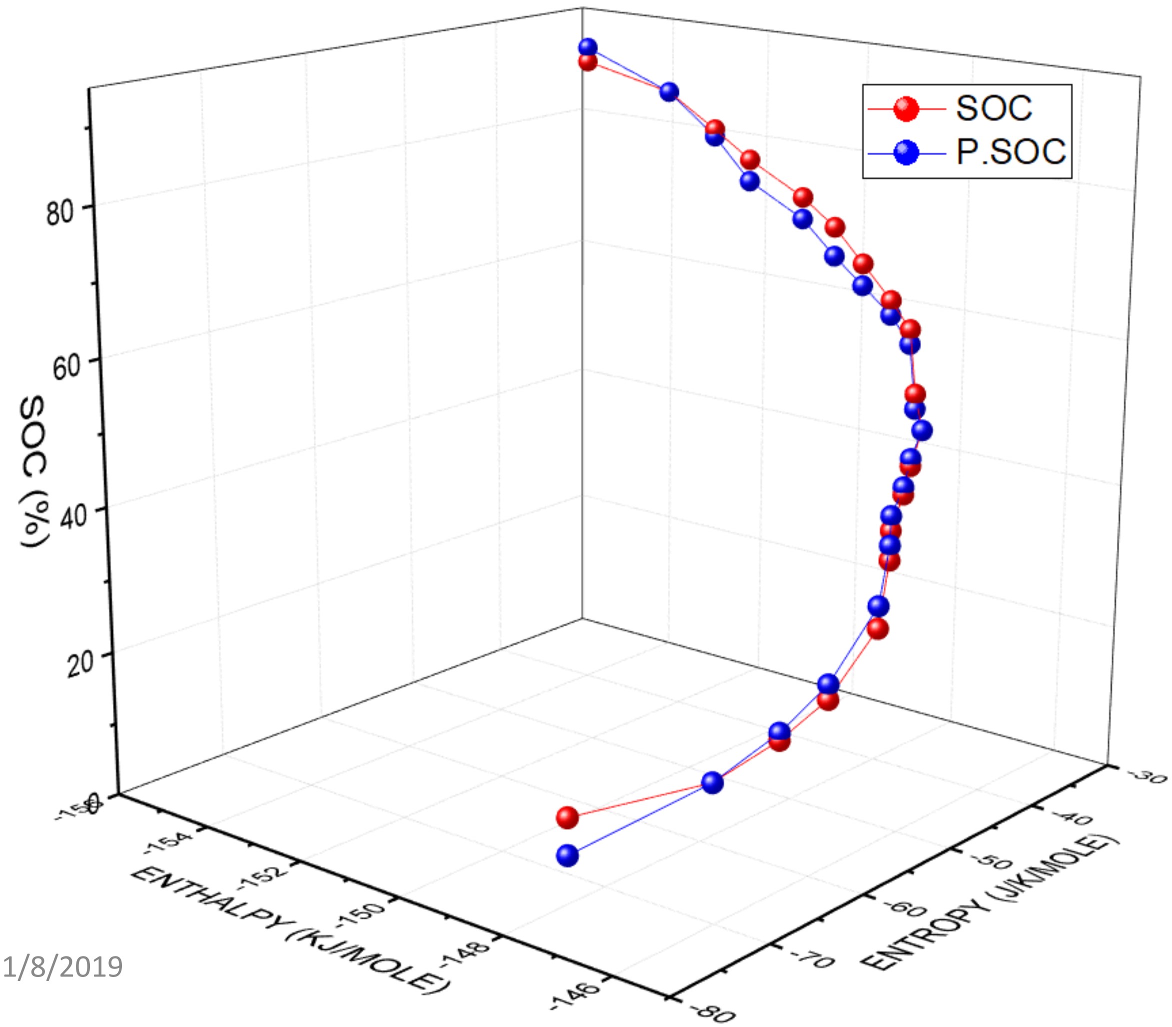
$\beta = 0.3708$

$\gamma = -4.510$

R^2=0.973

2. ZINC /CARBON DRY CELL

SOC simulation



$\alpha = -383.19$

$\beta = 1.595$

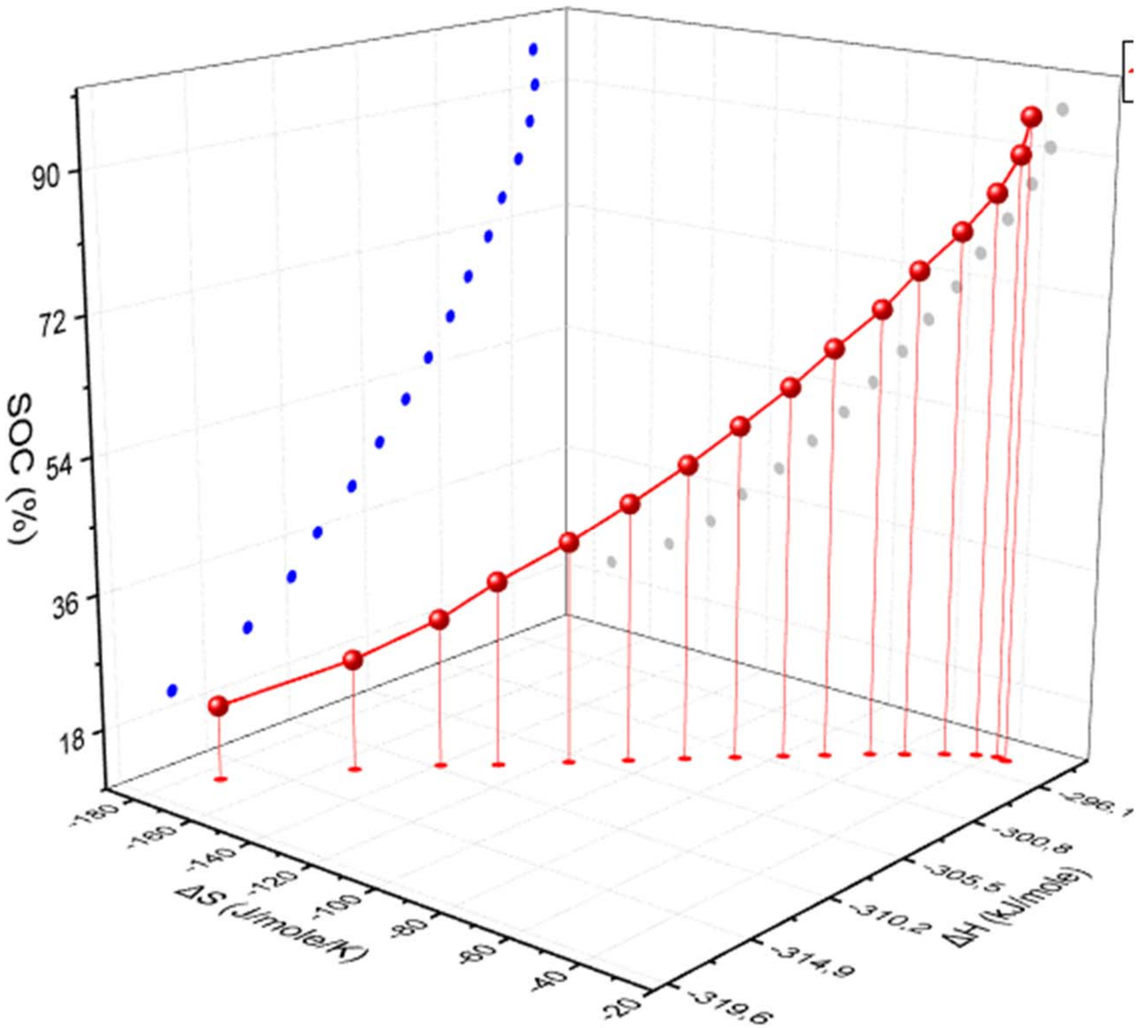
$\gamma = -3.414$

$R^2 = 0.987$

3. Lithium (primary) cells

a. Li/MnO_2 cells

3D plots



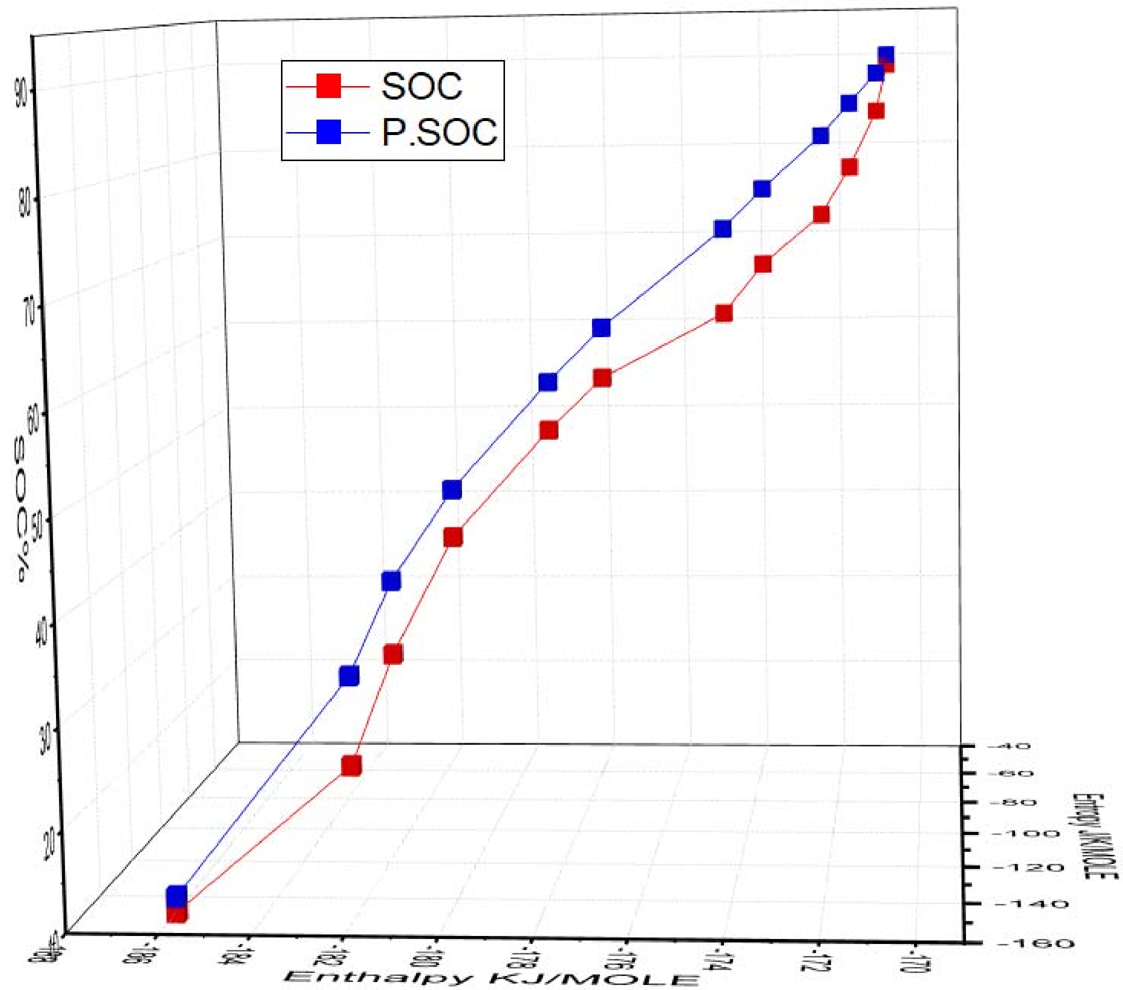
$\alpha = -1800$

$\beta = 1.611$

$\gamma = -6.627$

$R^2 = 0.9982$

b. Li-FeS_2 cells



$\alpha = 167$

$\beta = 0.8$

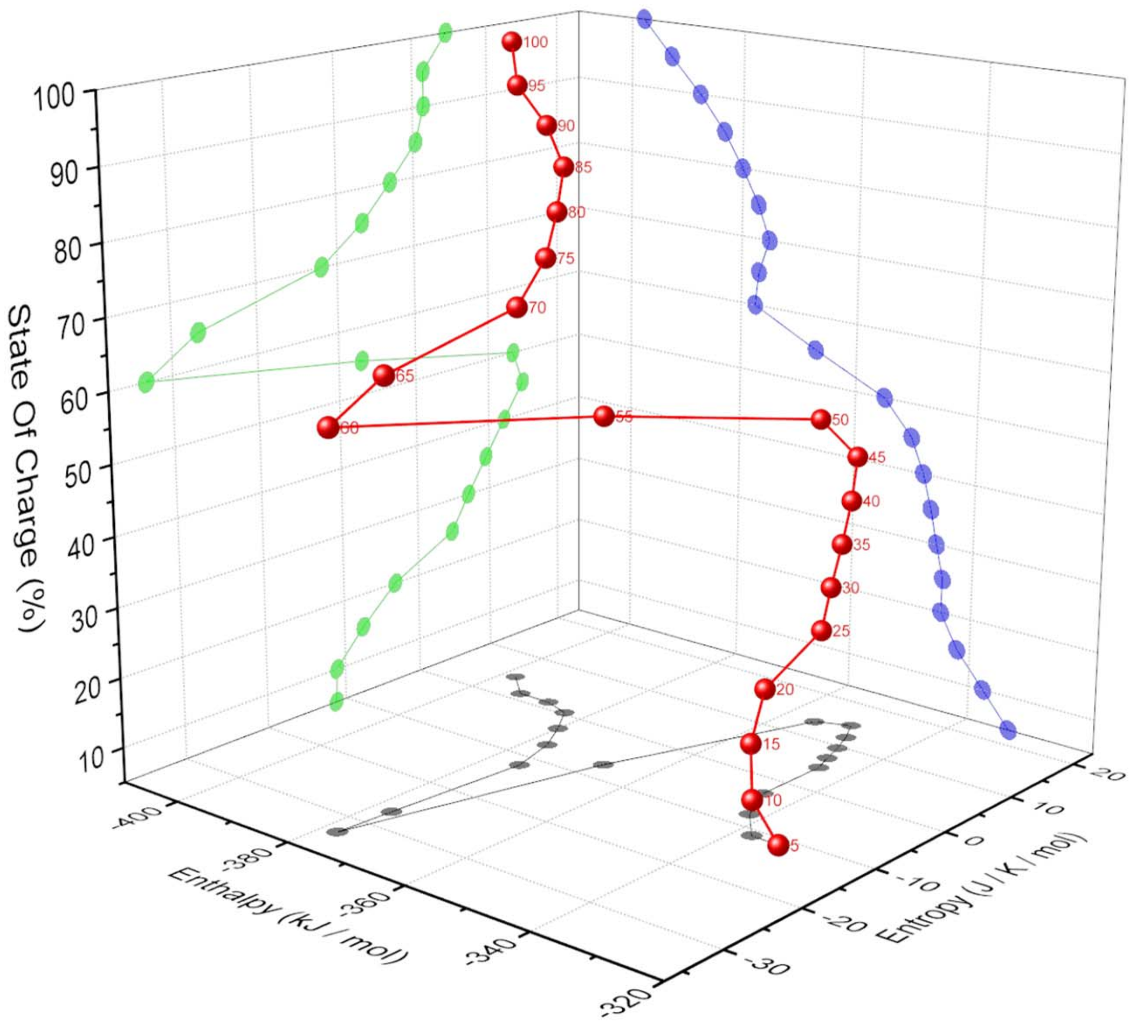
$\gamma \;\; = 0.2$

$R^2 = \;\; 0.98$

2. RECHARGEABLE CELLS

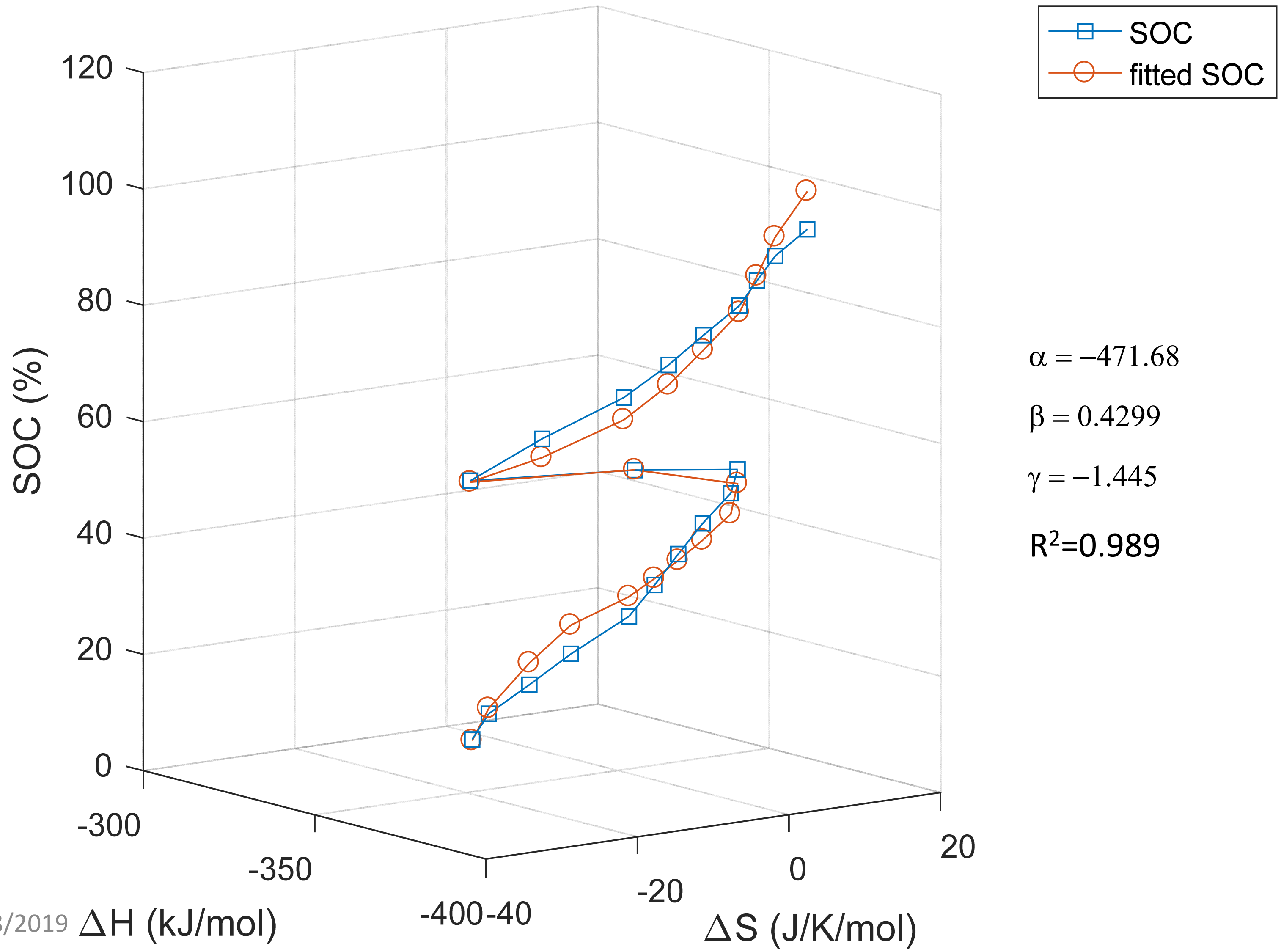
a. Lithium Ion Batteries

SOC-ΔS-ΔH 3D plots



SOC Simulation

SOC= α +$\beta\Delta$S +$\gamma\Delta$H



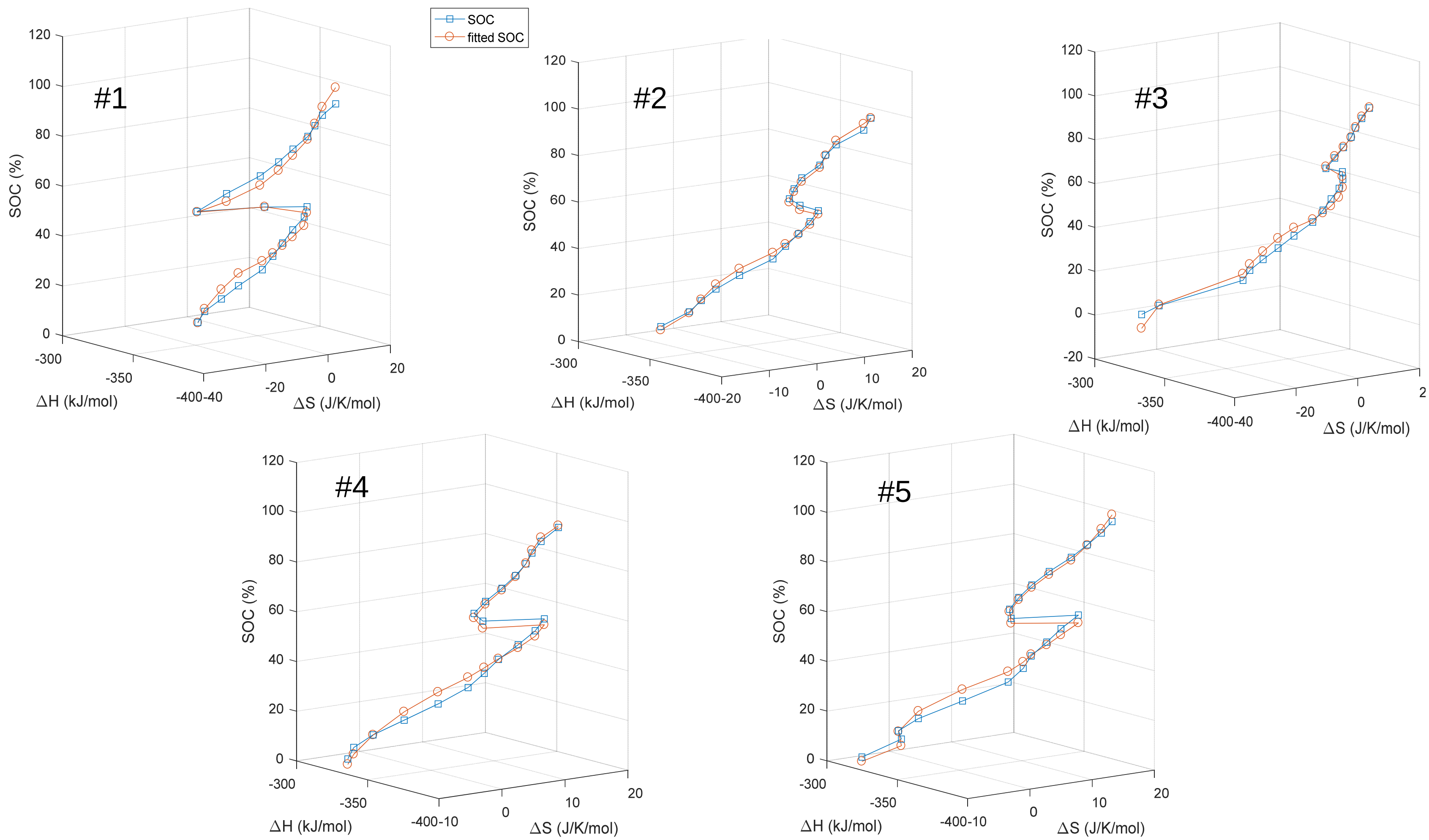
$\alpha = -471.68$

$\beta = 0.4299$

$\gamma = -1.445$

R^2=0.989

Linear relationship applies to all LIB chemistries

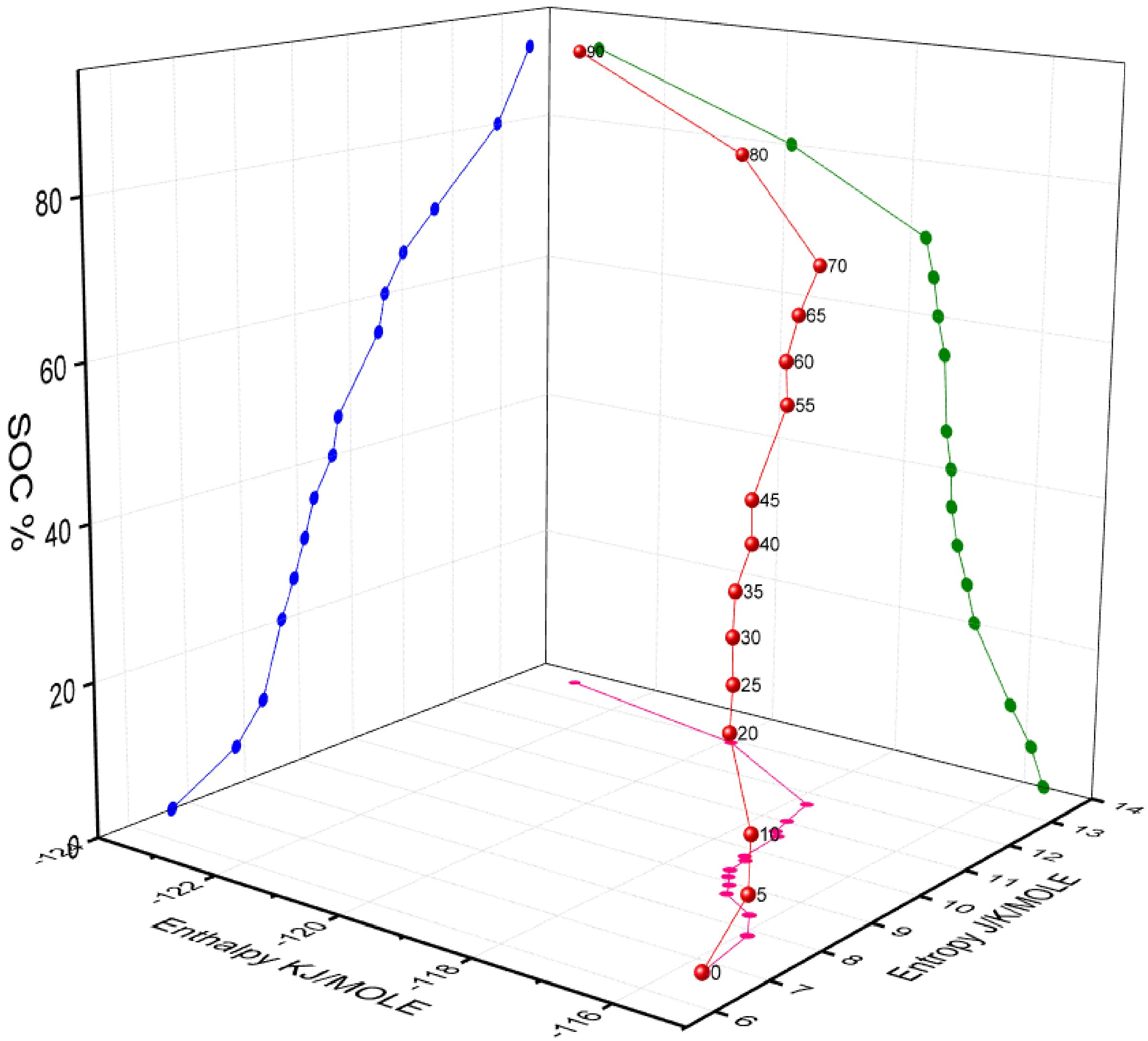


SOC fitting parameters for # LIBs

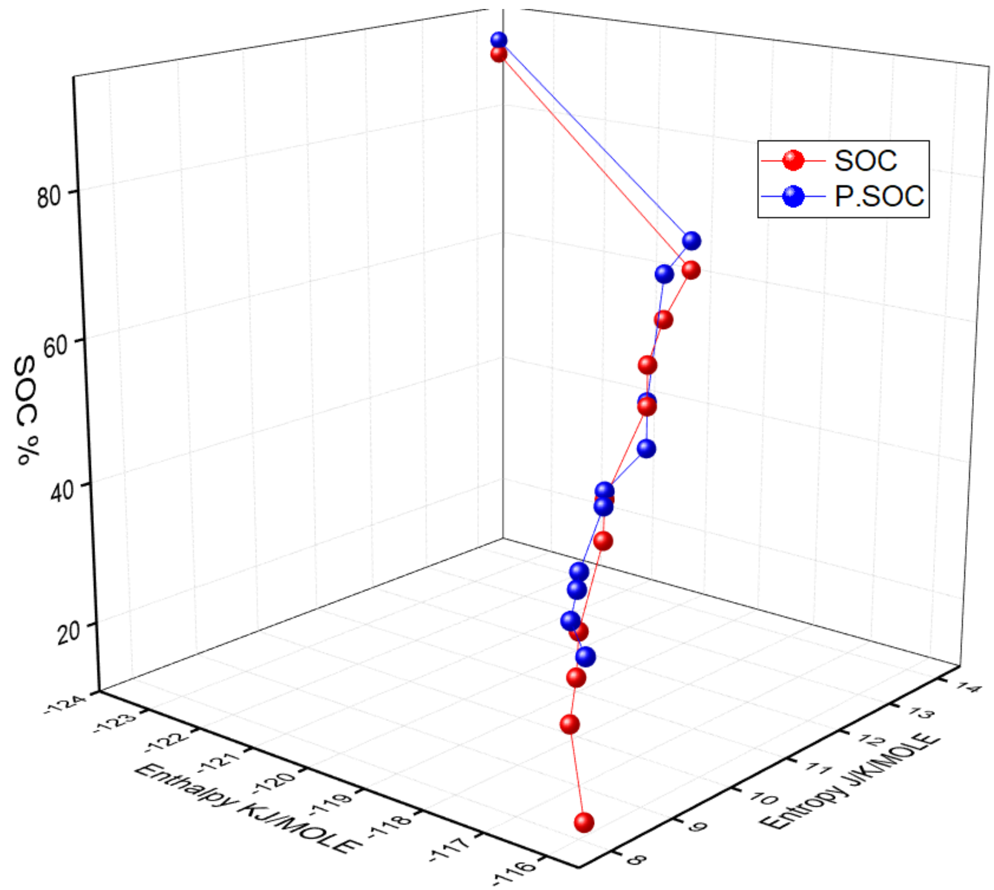
Battery #	α	β	γ	R^2
1	-471.6797	0.4299	-1.4449	**0.989**
2	-422.2317	0.7183	-1.3116	**0.996**
3	-438.1669	0.3607	-1.3688	**0.991**
4	-445.4292	0.6906	-1.3734	**0.994**
5	-423.5349	0.4894	-1.3335	**0.994**

b. Ni-MH

SOC-ΔS-ΔH 3D plots Ni-MH



SOC Simulation



Battery #	α	β	γ	R^2
1	–503.7	8.5	–3.8	0.85

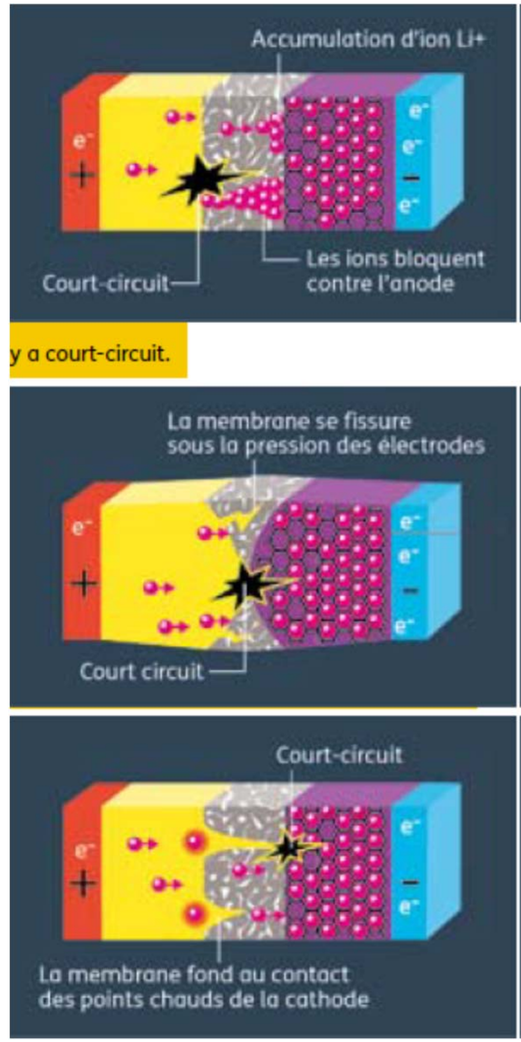
3. SOH assessment

α, β *and* γ depend on SOH

Cycle # (55 ºC, 1C-rate)	SOH (%)	α	β	γ	R^2
0	**100**	-523.56	0.31312	-1.6159	**0.99+**
50	**97.7**	-453.82	0.08161	-1.4162	
100	**92.9**	-438.82	0.15153	-1.3736	
150	**91.5**	-417.76	0.024905	-1.3119	
200	**89.5**	-414.18	0.081835	-1.3004	
50	**88.5**	-432.2	0.15816	-1.3561	
300	**86.6**	-390.2	0.095205	-1.2439	
350	**84.7**	-434.42	0.18258	-1.3638	

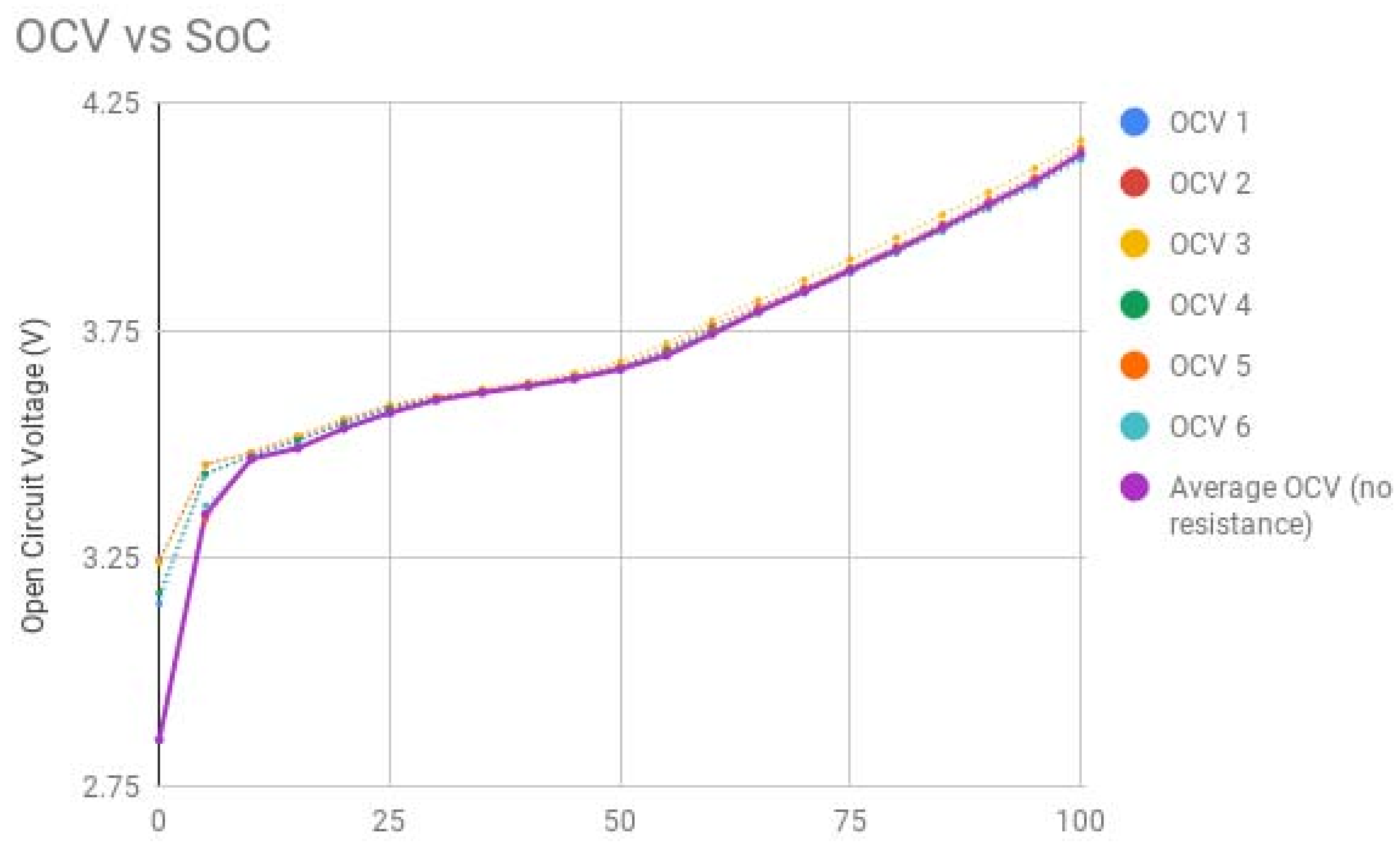
4. SOS assessment

Internal short-circuit model for thermal runaway

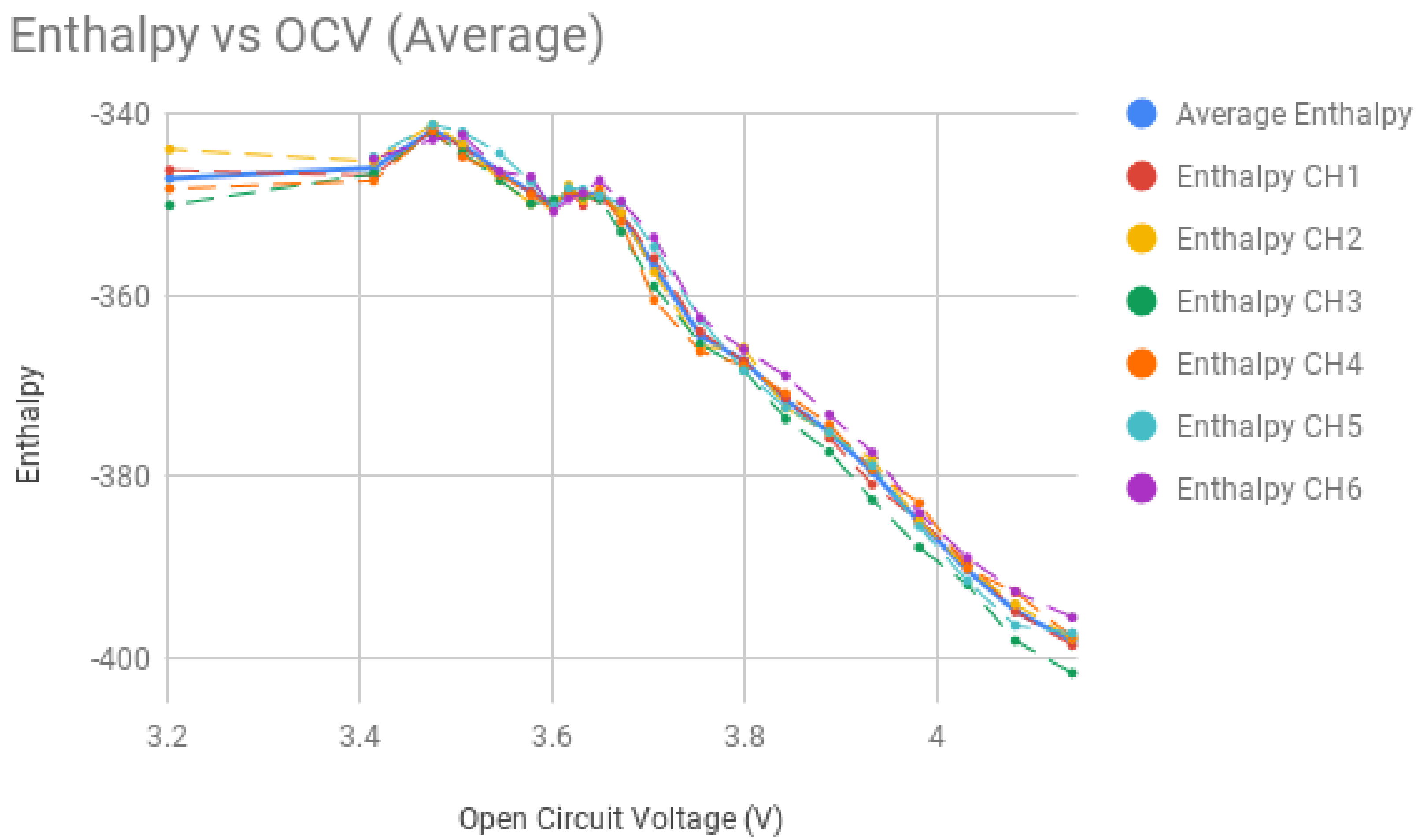


4. SOS assessment

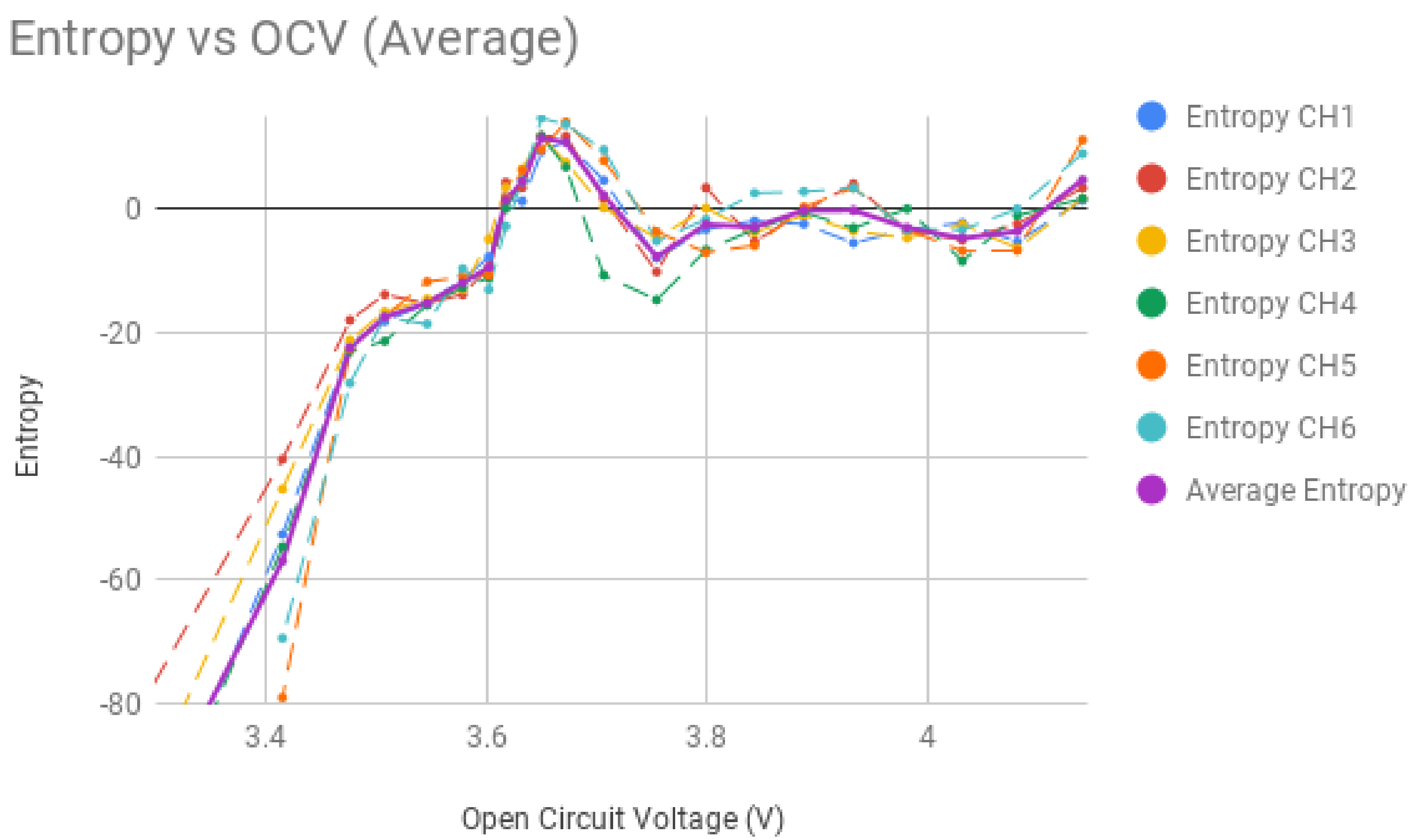
Internal Short-Circuit Detection



4. SOS assessment

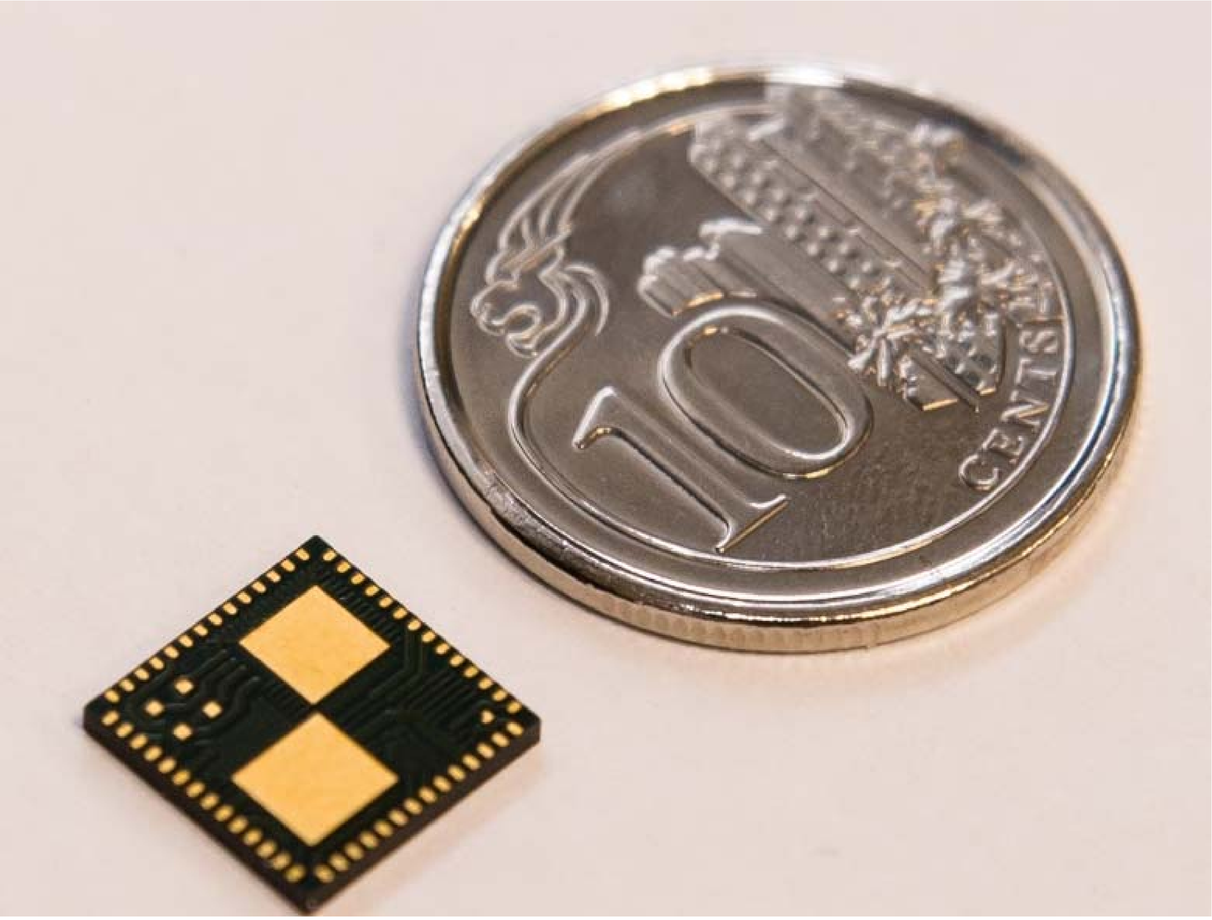


4. SOS assessment



Confidential

The Imbedded Chip for online SOC, SOH and SOS online assessment



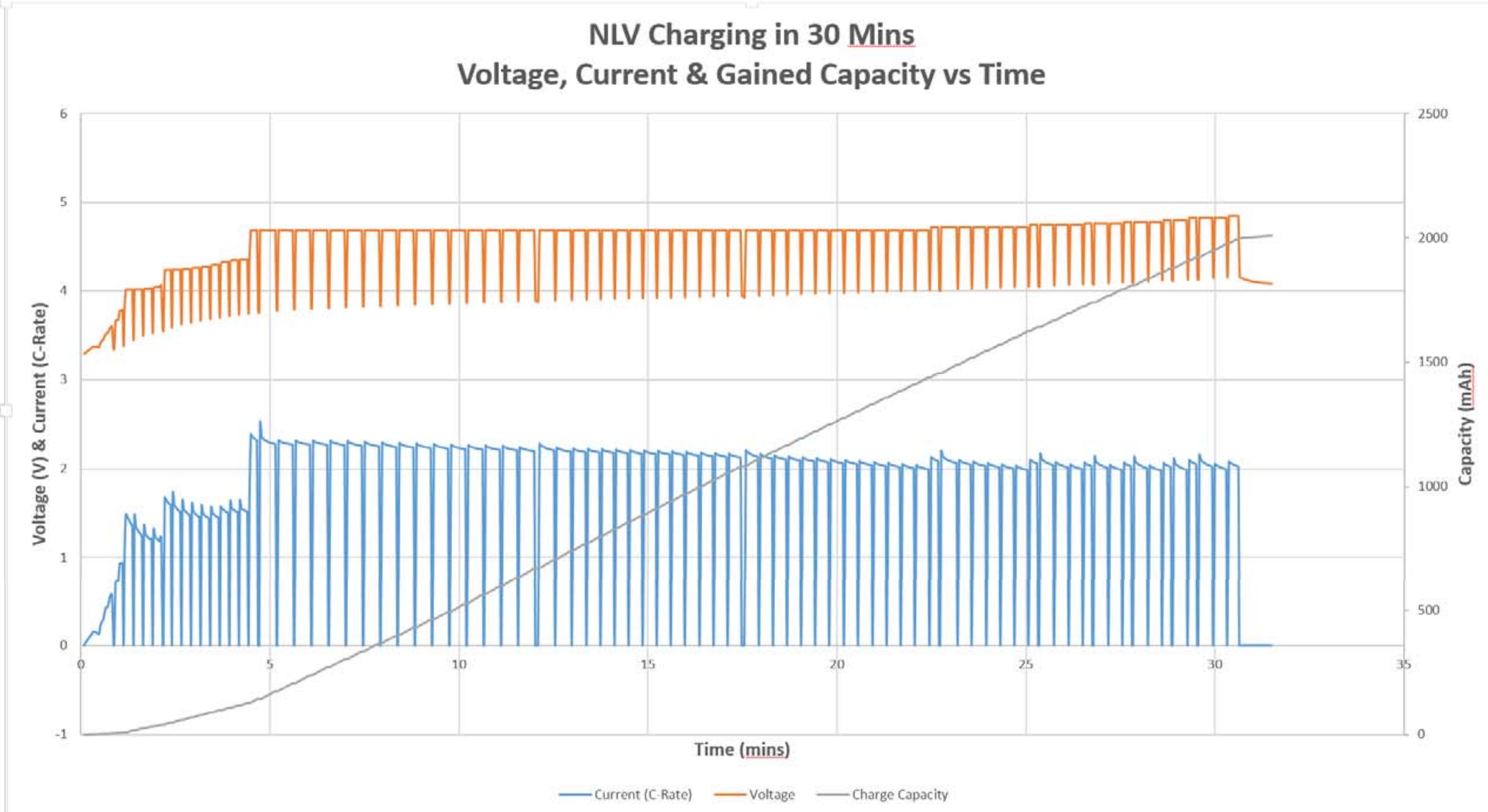
5. Fast charging: beyond CCCV

a. Non-linear voltammetry (NLV)

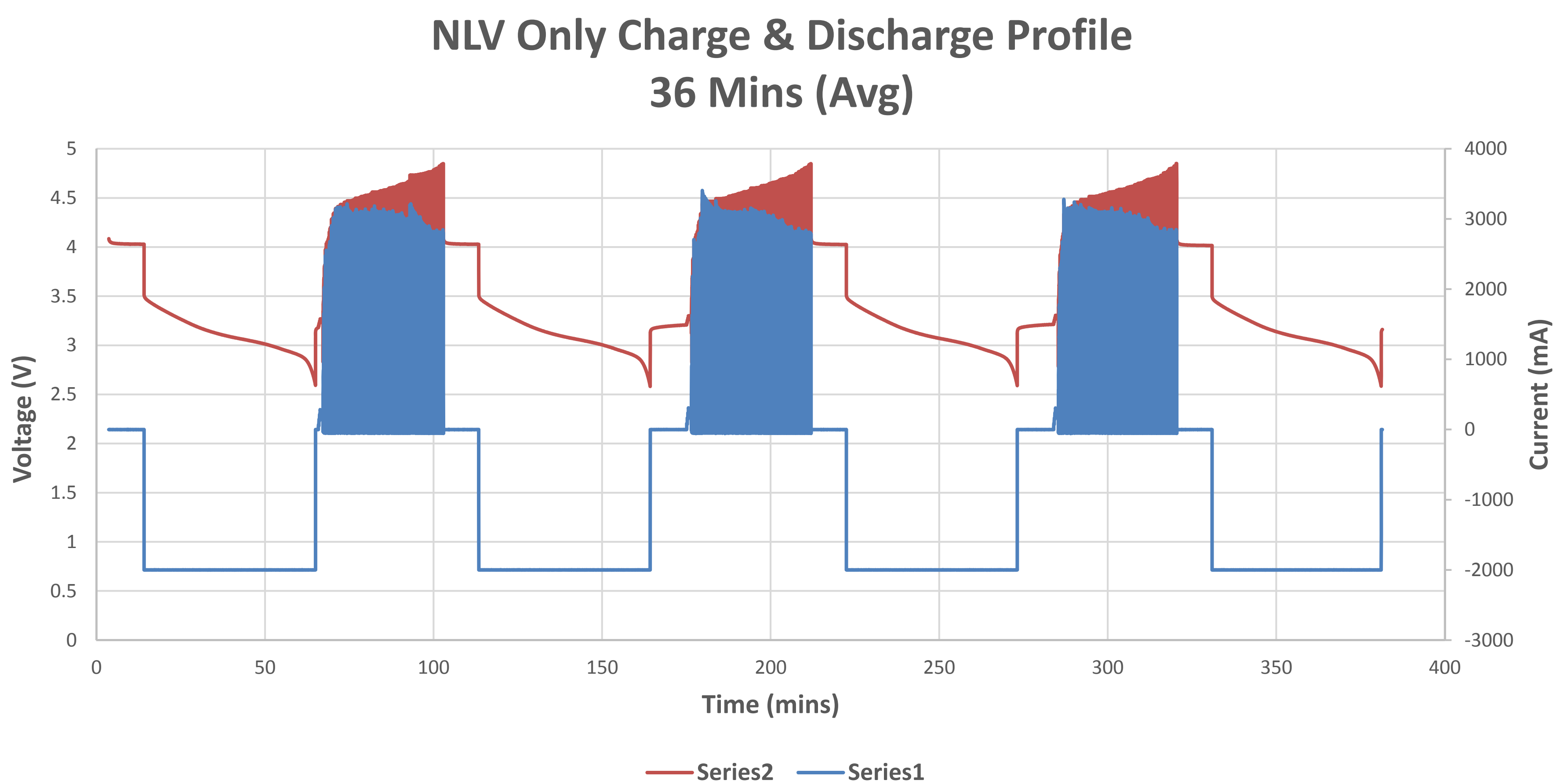
Solving a differential equation:

$$\boldsymbol{\phi}\left(i, v, \frac{\partial i}{\partial t}, \frac{\partial v}{\partial t}, \mathbf{SOH}\right) = \mathbf{0}$$

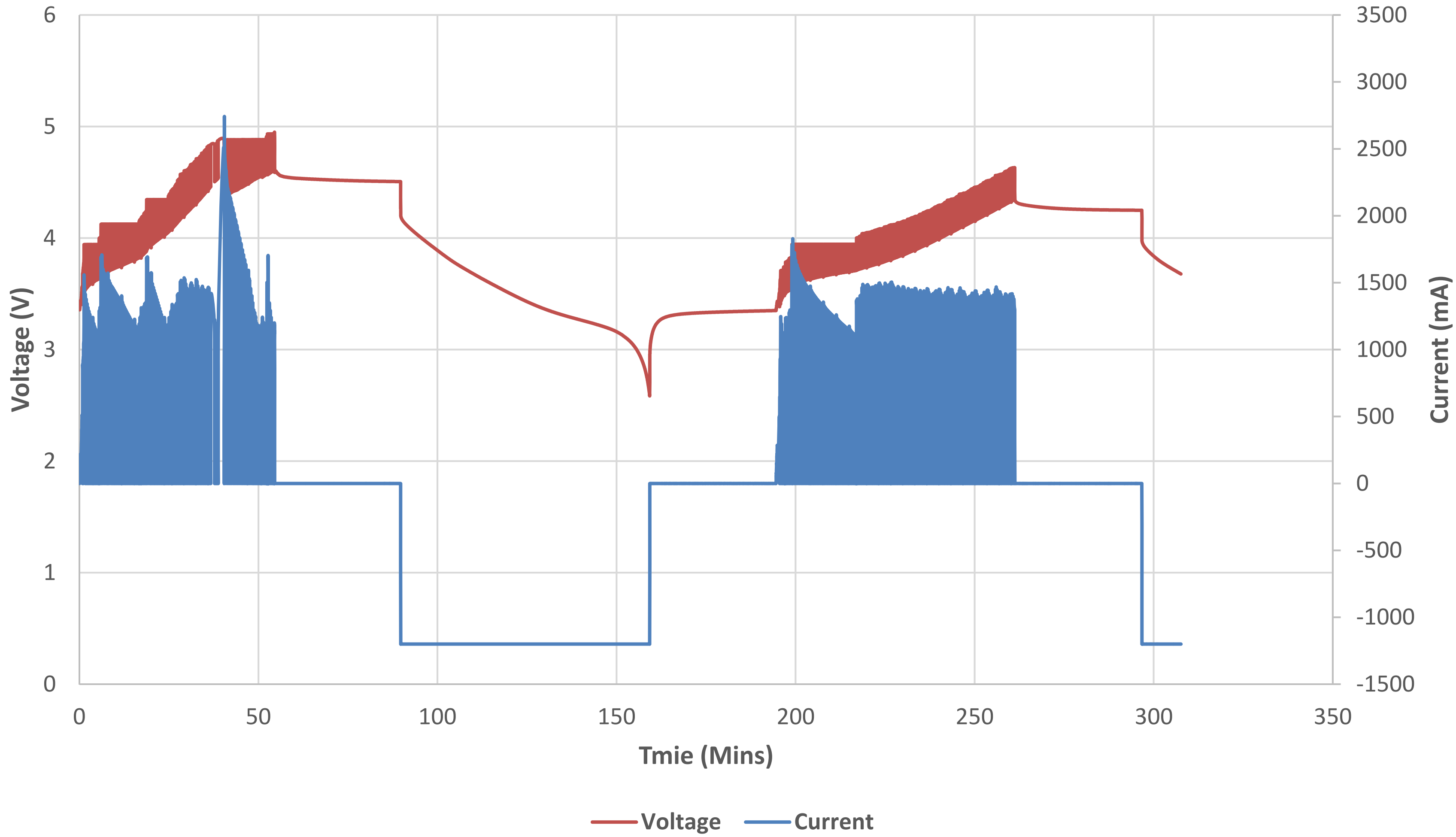
Typical current, voltage, capacity profiles during NLV charging



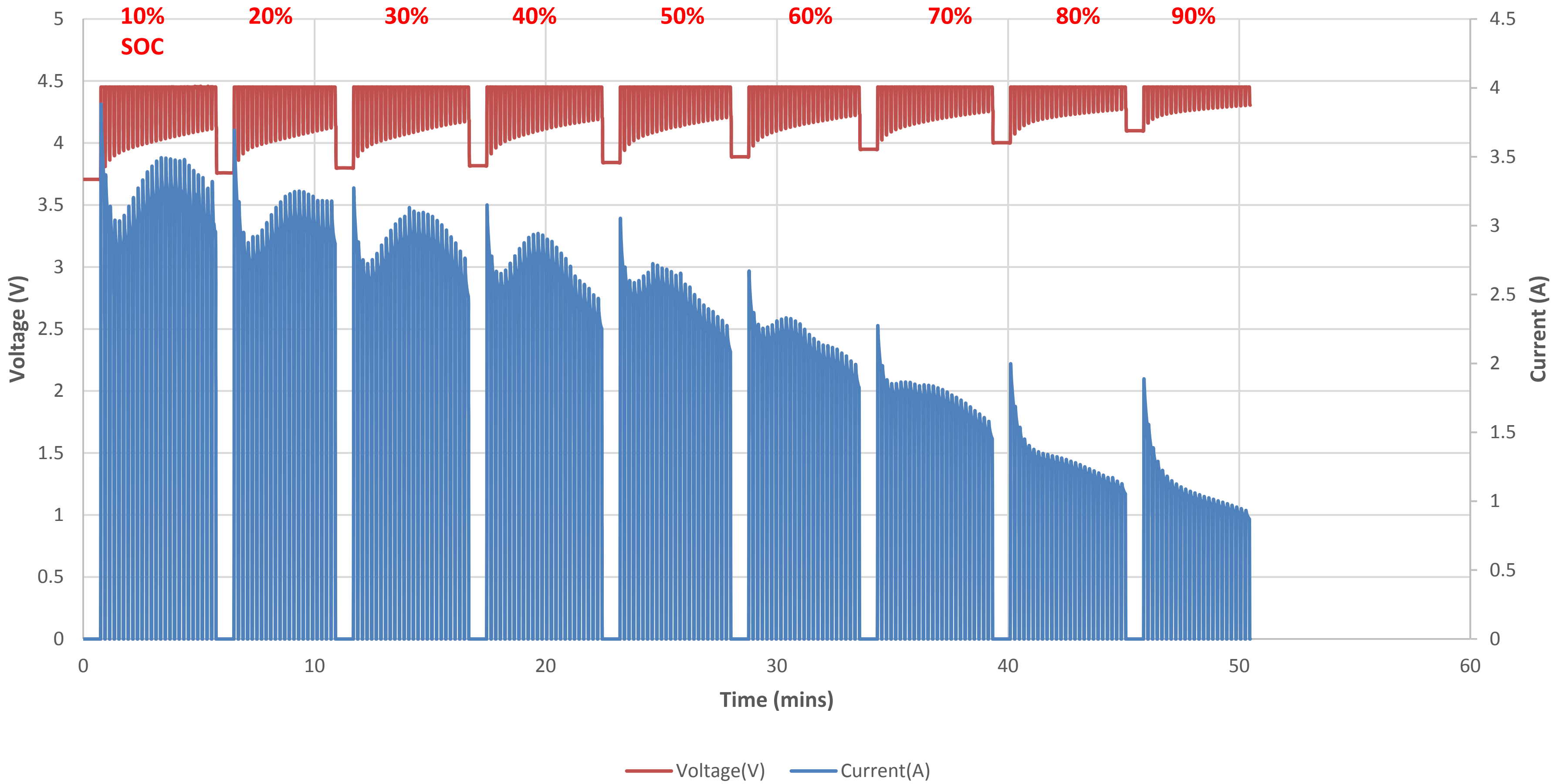
Charge-discharge profiles



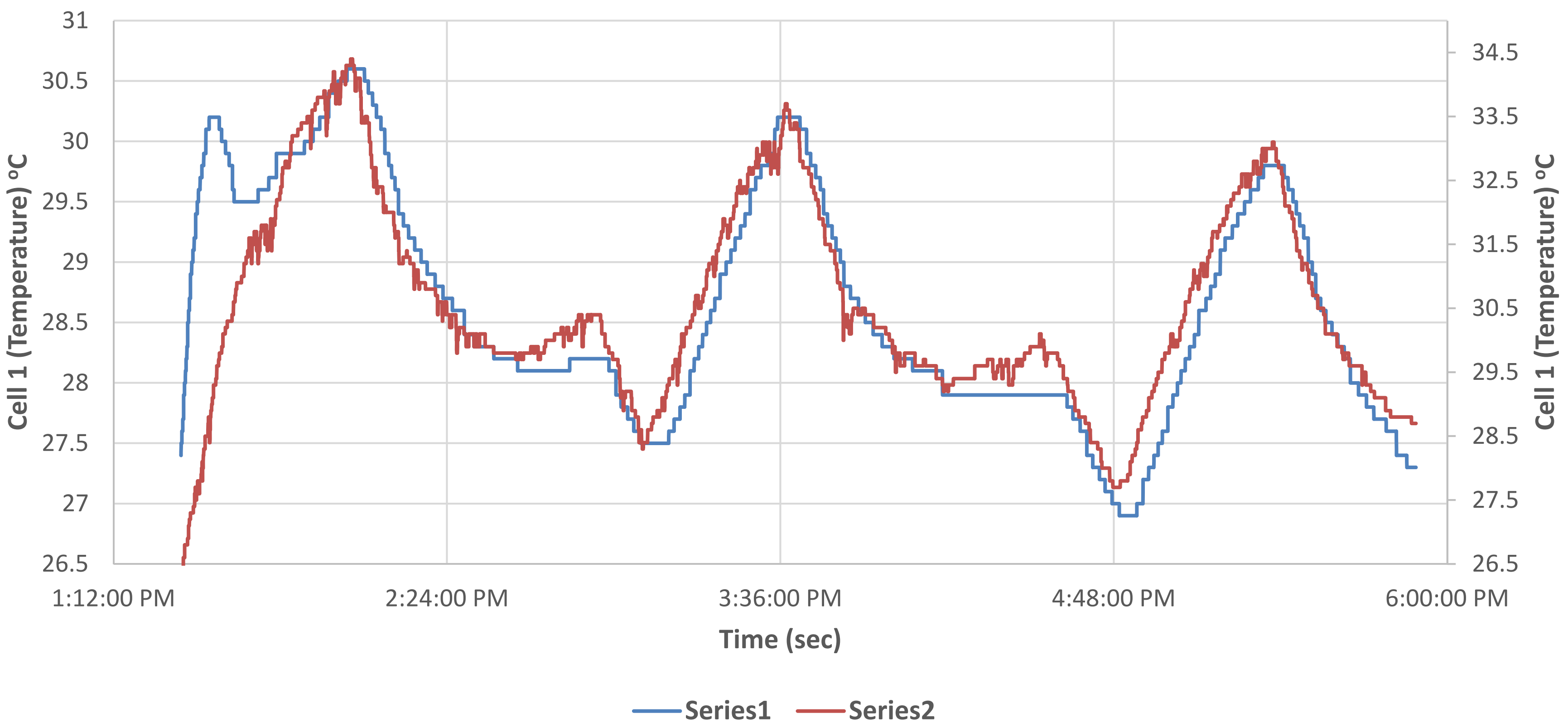
Charge profile may be different at each cycle



Intermittent NLV charge profile

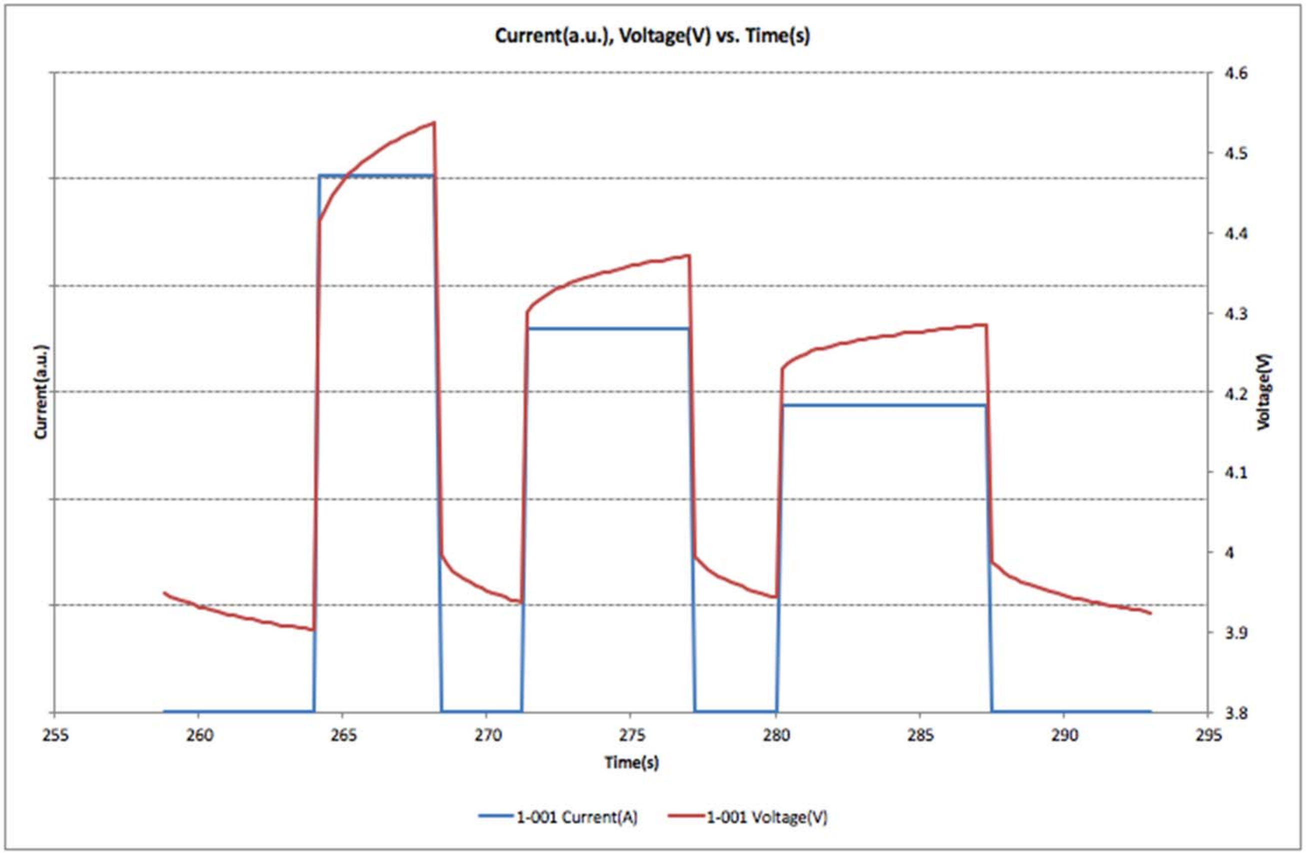


Temperature Profile

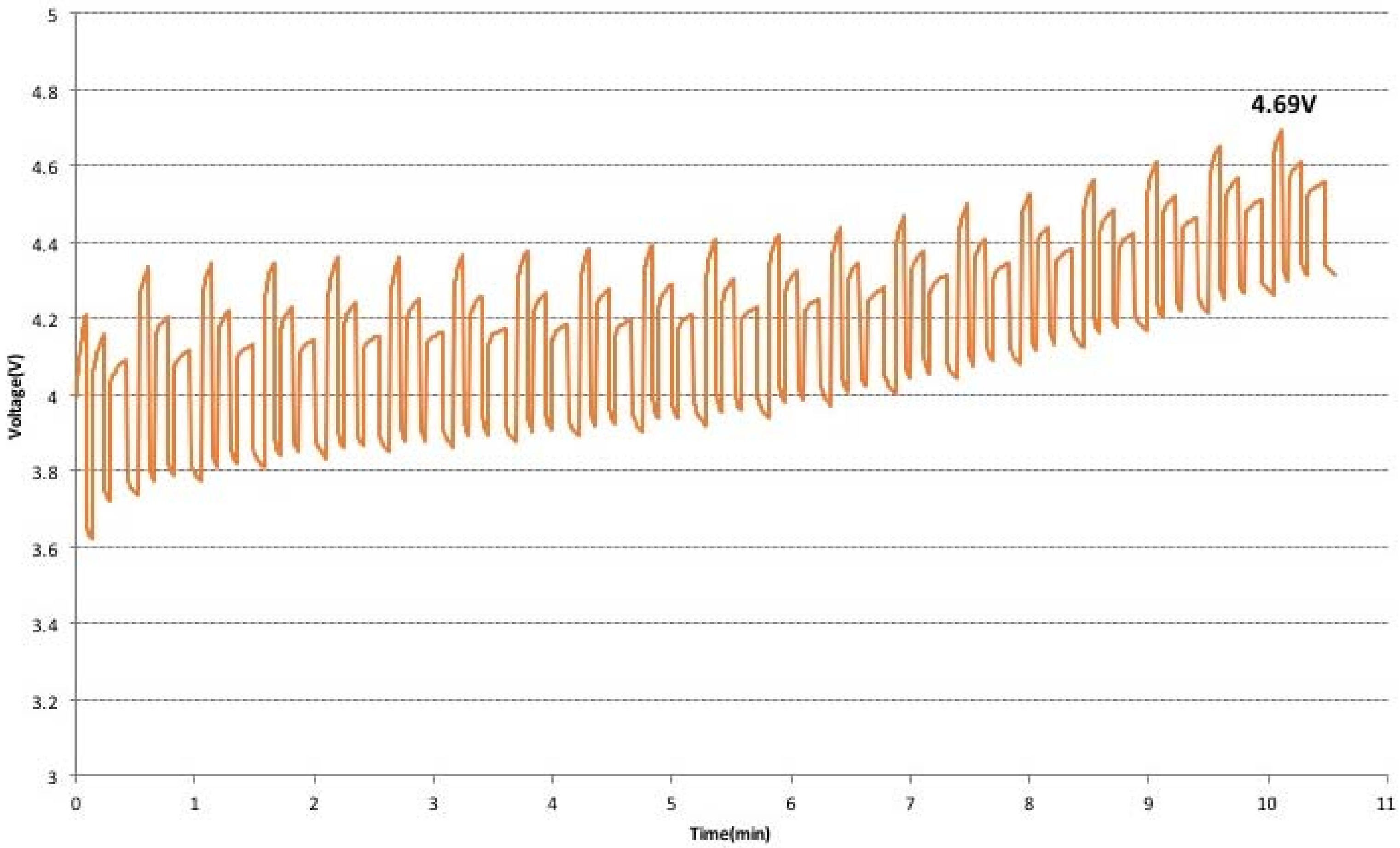


5. Fast charging: CPC

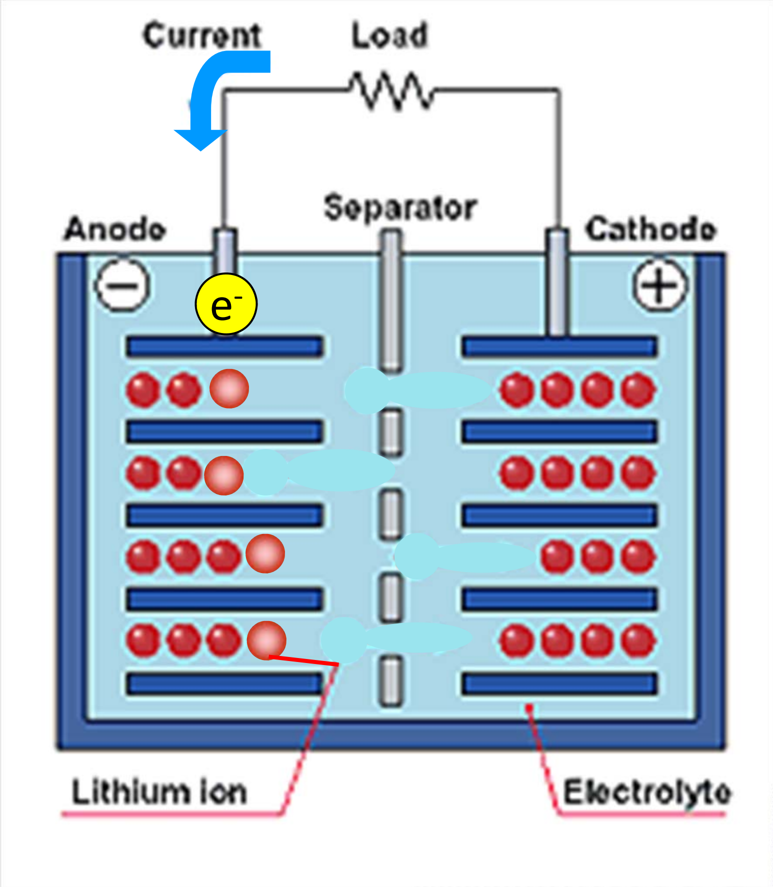
b. Cascade Pulse Charge



CPC in 10 min: voltage profile



Introduction: electrode processes in LIB



Theoretical lithium composition in anode and cathode in a C/LCO cell

	Charge state	Discharge state	Capacity (mAh/g)
Graphite anode	LiC_6	Li_0C_6	372
LCO cathode	$Li_{0.5}CoO_2$	$LiCoO_2$	138

Ideal cell reaction:

$$0.5Li_0C_6 + LiCoO_2 \leftrightarrow 0.5LiC_6 + Li_{0.5}CoO_2$$

Theoretical lithium composition in anode and cathode vs. SOC of a C/LCO cell

X=SOC of the full cell,

$0 \le X \le 100\%$; $0 \le x = \frac{X}{100} \le 1$

- Anode composition: Li_xC_6
- Cathode composition: $Li_{1-\frac{x}{2}}CoO_2$

Question: What is the actual Li composition in anode and cathode vs. SOC in a real cell?

- Anode composition: $Li_{f(X)}C_6$,
- Cathode composition: $Li_{g(X)}MO_2$,

What is f(X)?, g(X)?

A very simple question,
NO EXISTING ANSWER TODAY !

Why no answer?

- There are 4 unknowns

$$x_{min}, x_{max} \text{ and } y_{min}, y_{max}$$

  - Cathode: x_{min}<g(X)<x_{max} in Li_xMO_2
  - Anode: y_{min}<f(X)<y_{max} in Li_yC_6

- We need 4 independent equations
  - OCV vs. SOC gives 1 equation
  - 3 equations are missing

Approach

At any SOC 'X' of a full cell, the following equations apply:

Free energy	$\Delta G(cell) = \Delta G^{+} - \Delta G^{-}$
Open-circuit potential	$E_0(cell) = E_0^{+} - E_0^{-}$
Entropy	$\Delta S(cell) = \Delta S^{+} - \Delta S^{-}$
Enthalpy	$\Delta H(cell) = \Delta H^{+} - \Delta H^{-}$

- Measure OCP, entropy and enthalpy in half-cells and in a full cell
- Fit OCP, entropy and enthalpy data vs. SOC
- Fit entropy and enthalpy data vs. OCP
  - Determine $\alpha_{ca}, \beta_{ca}, \alpha_{an}, \beta_{an}$ in the 2 equations

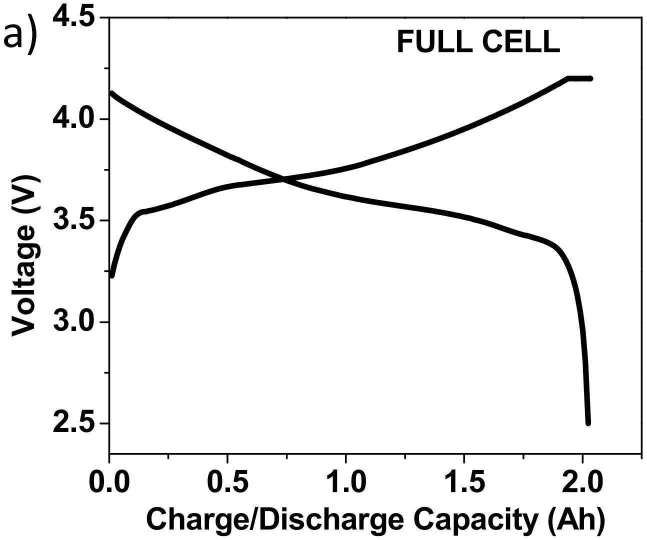
g(X)=$x = \alpha_{ca}X + \beta_{ca}$

f(X)=$y = \alpha_{an}X + \beta_{an}$

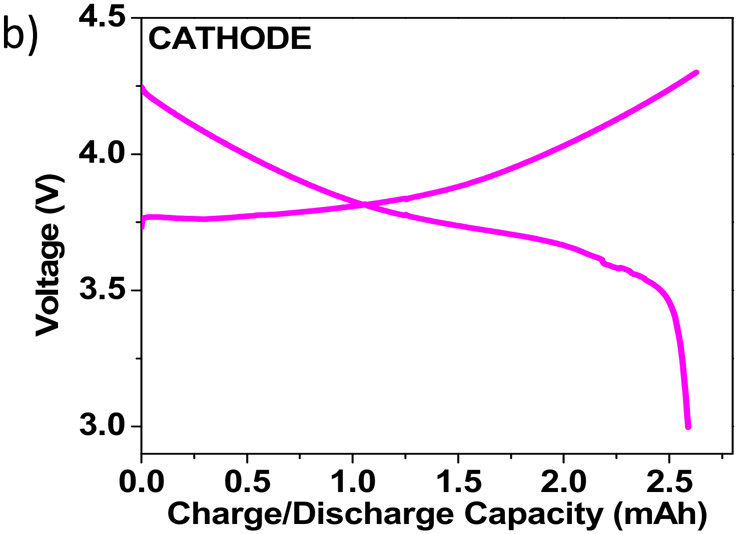
→ $x_{min}, x_{max}\ , \ y_{min}, y_{max}$

1. OCP profiles

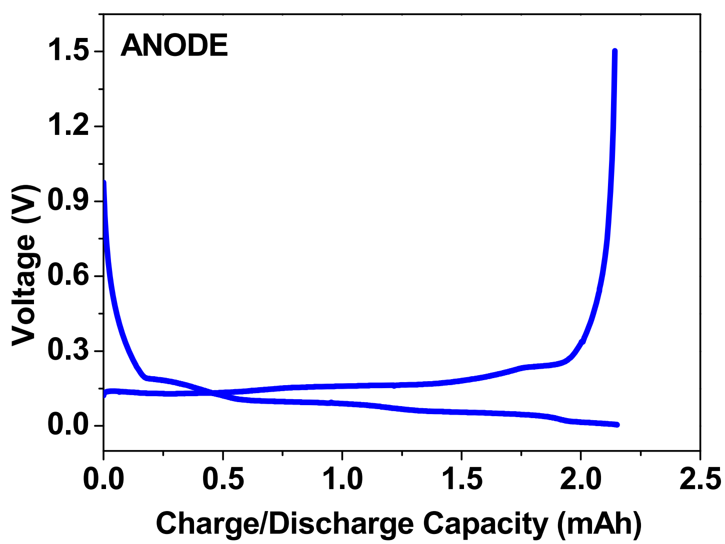
a)



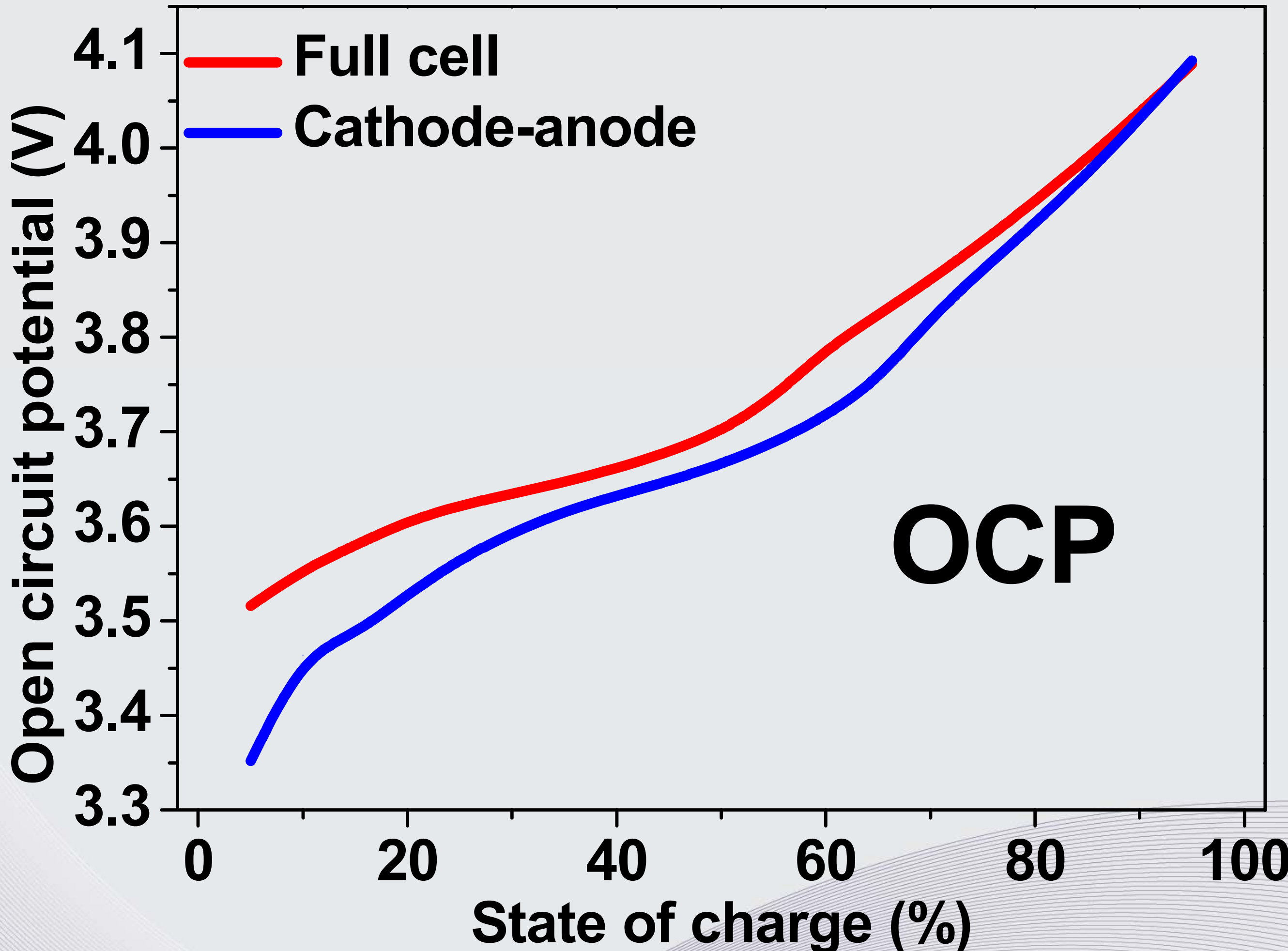
b)



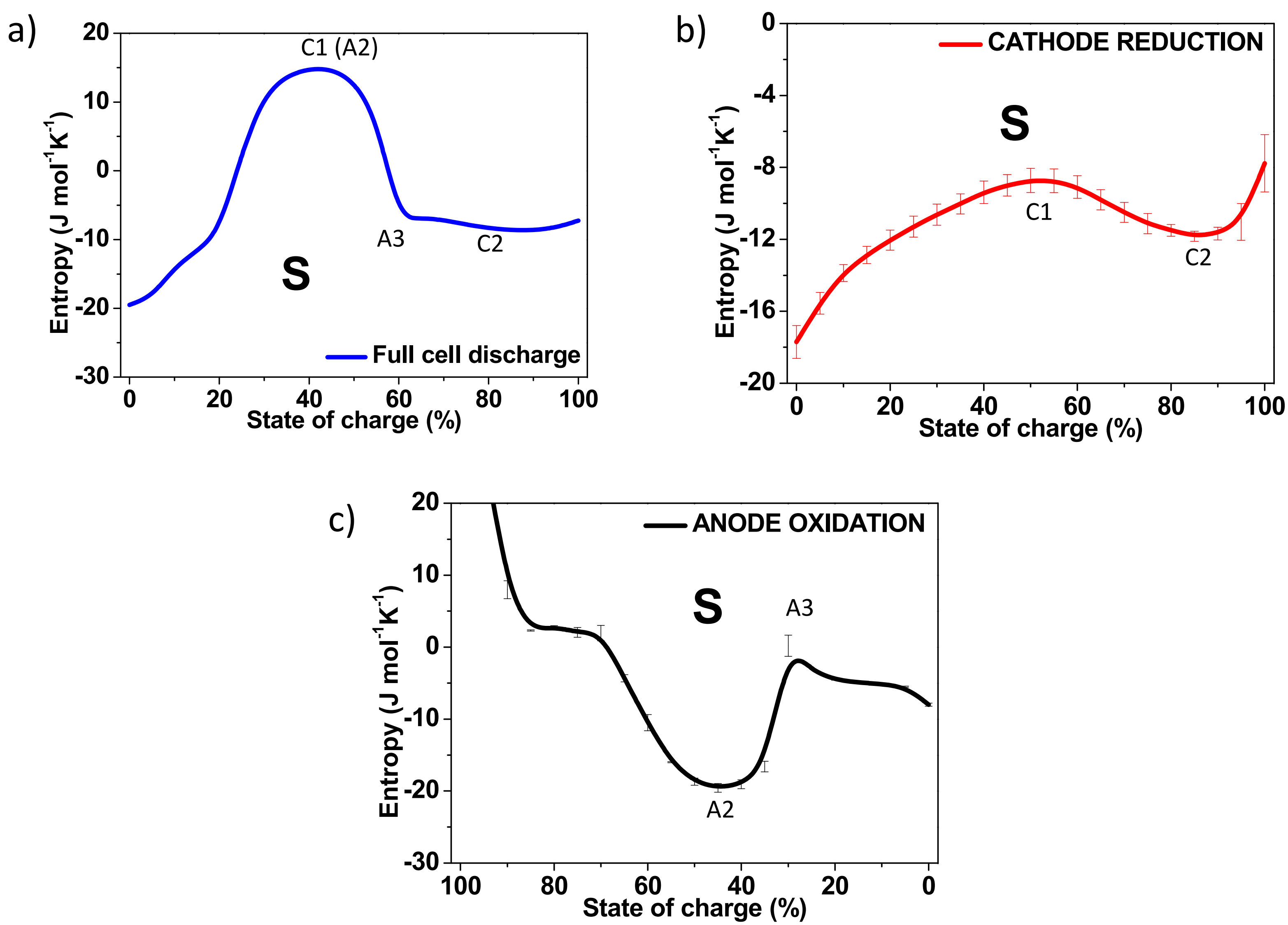
c)



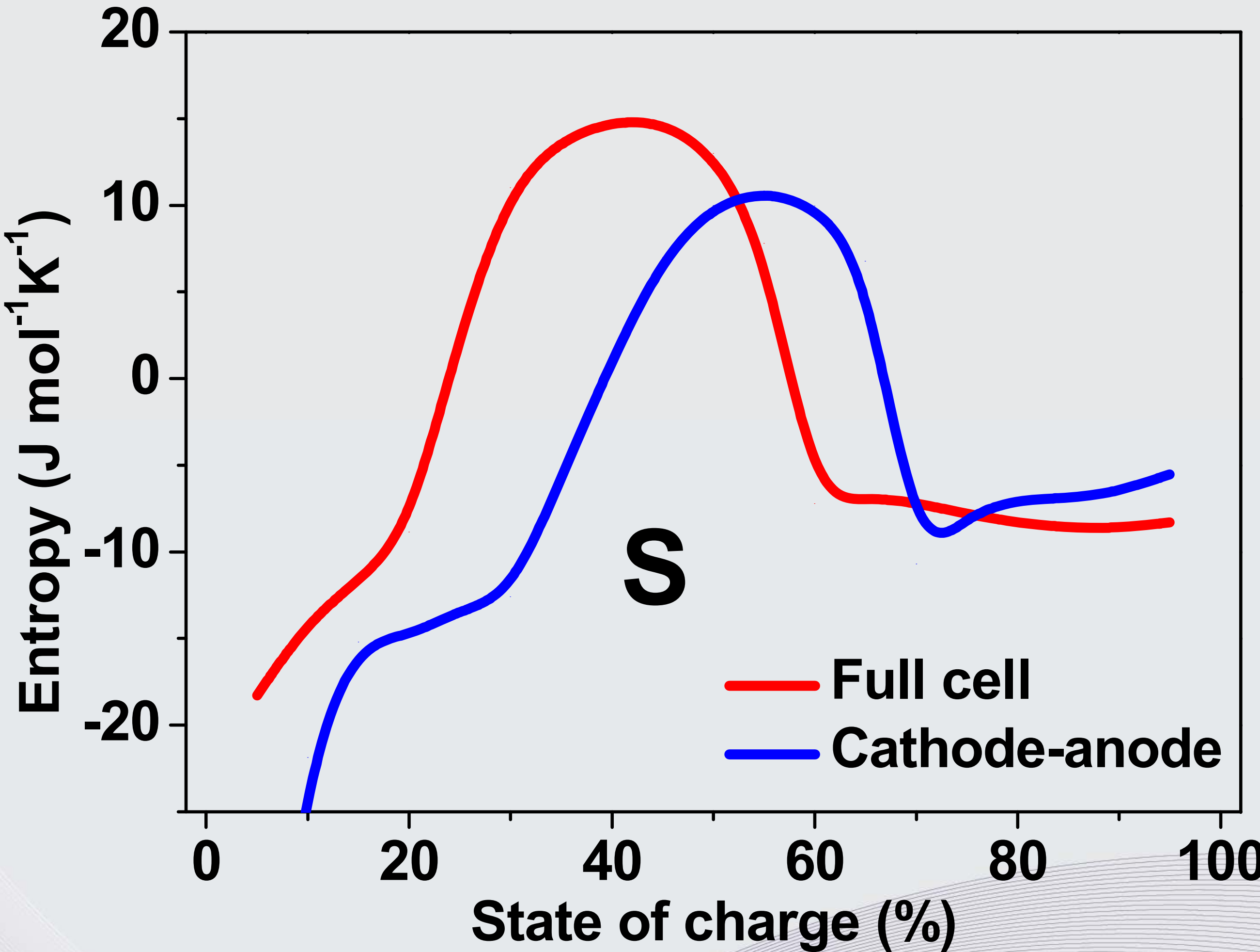
1. OCP mismatch



2. Entropy profiles

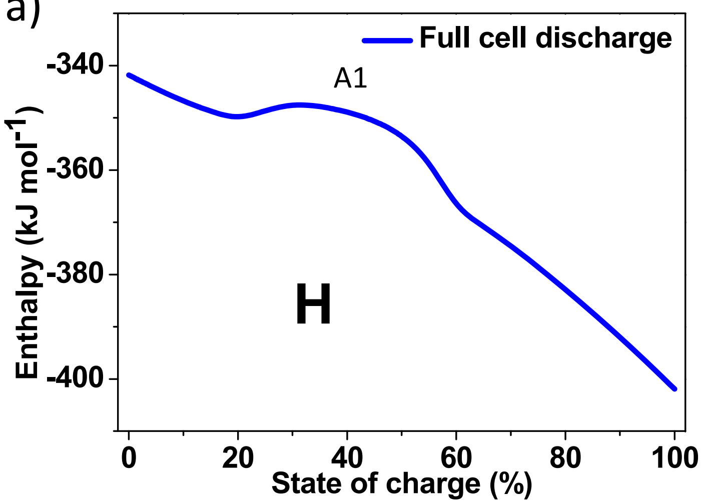


2. Entropy mismatch

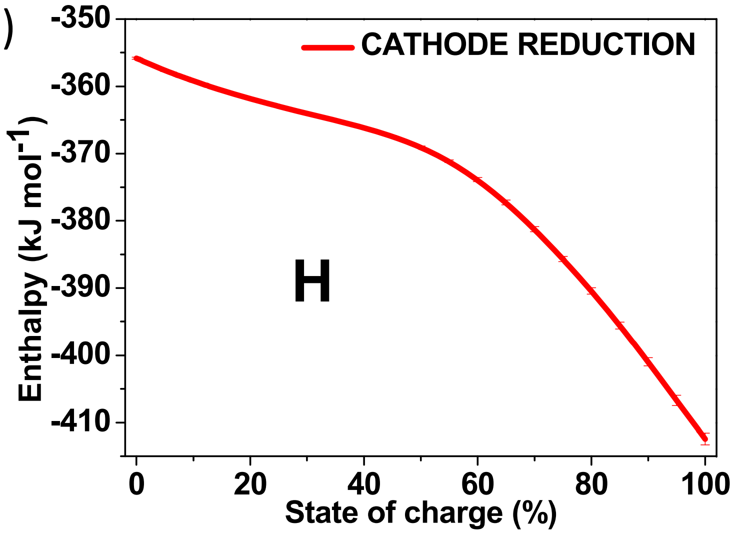


3. Enthalpy profiles

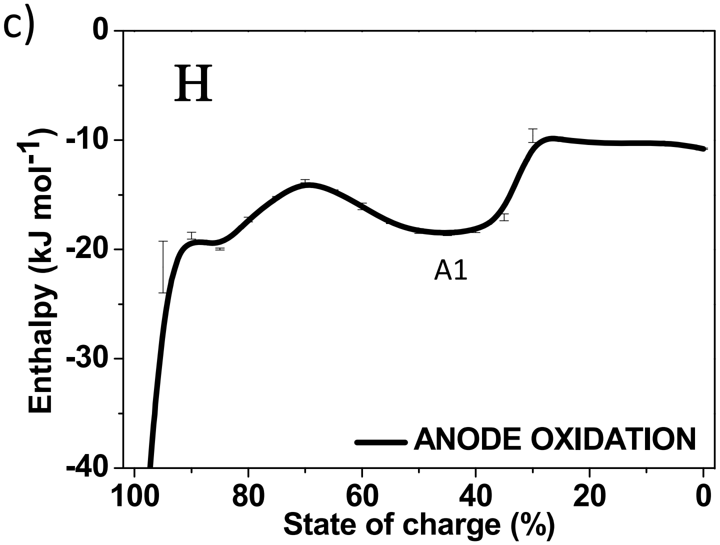
a)



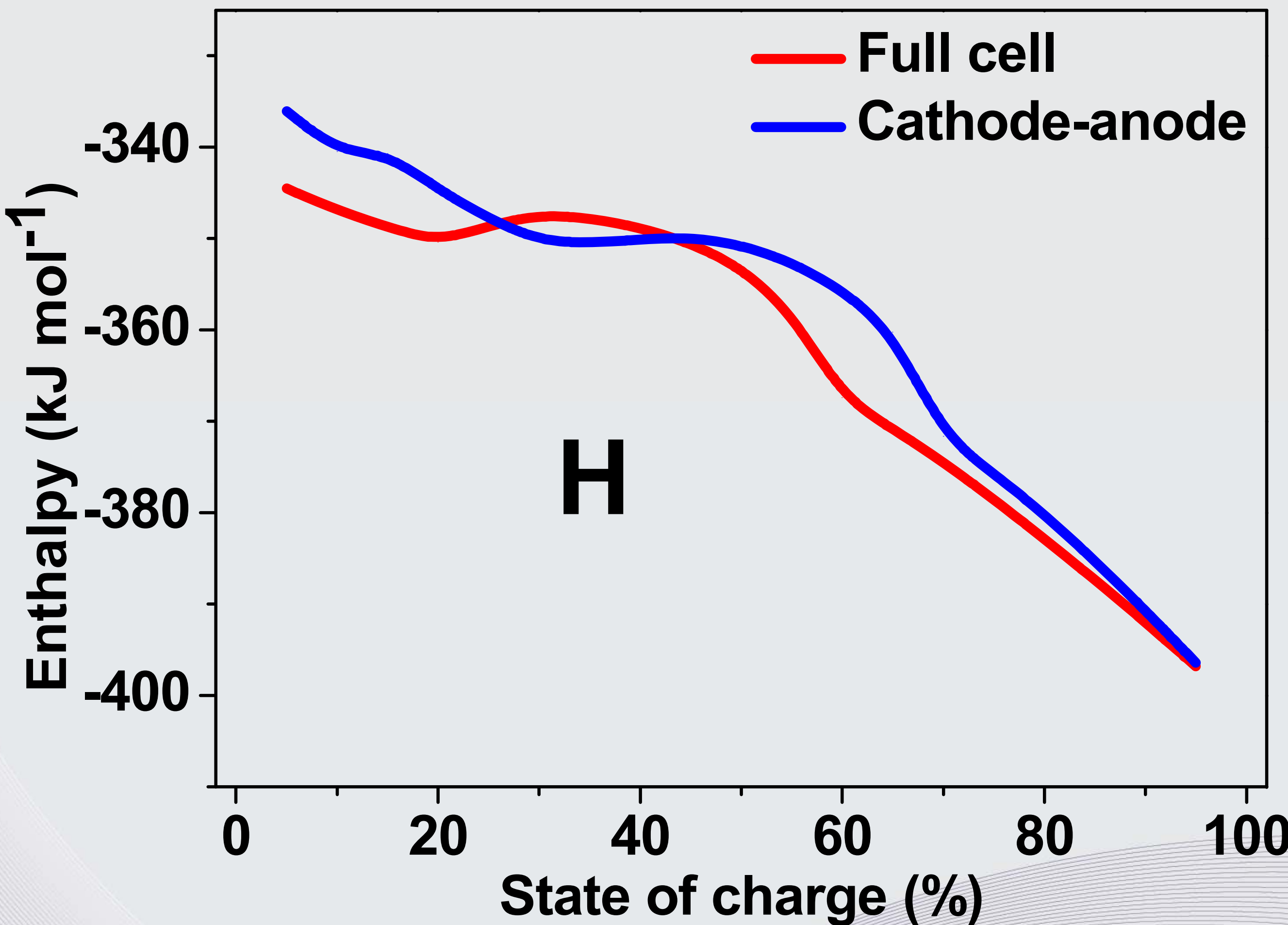
b)



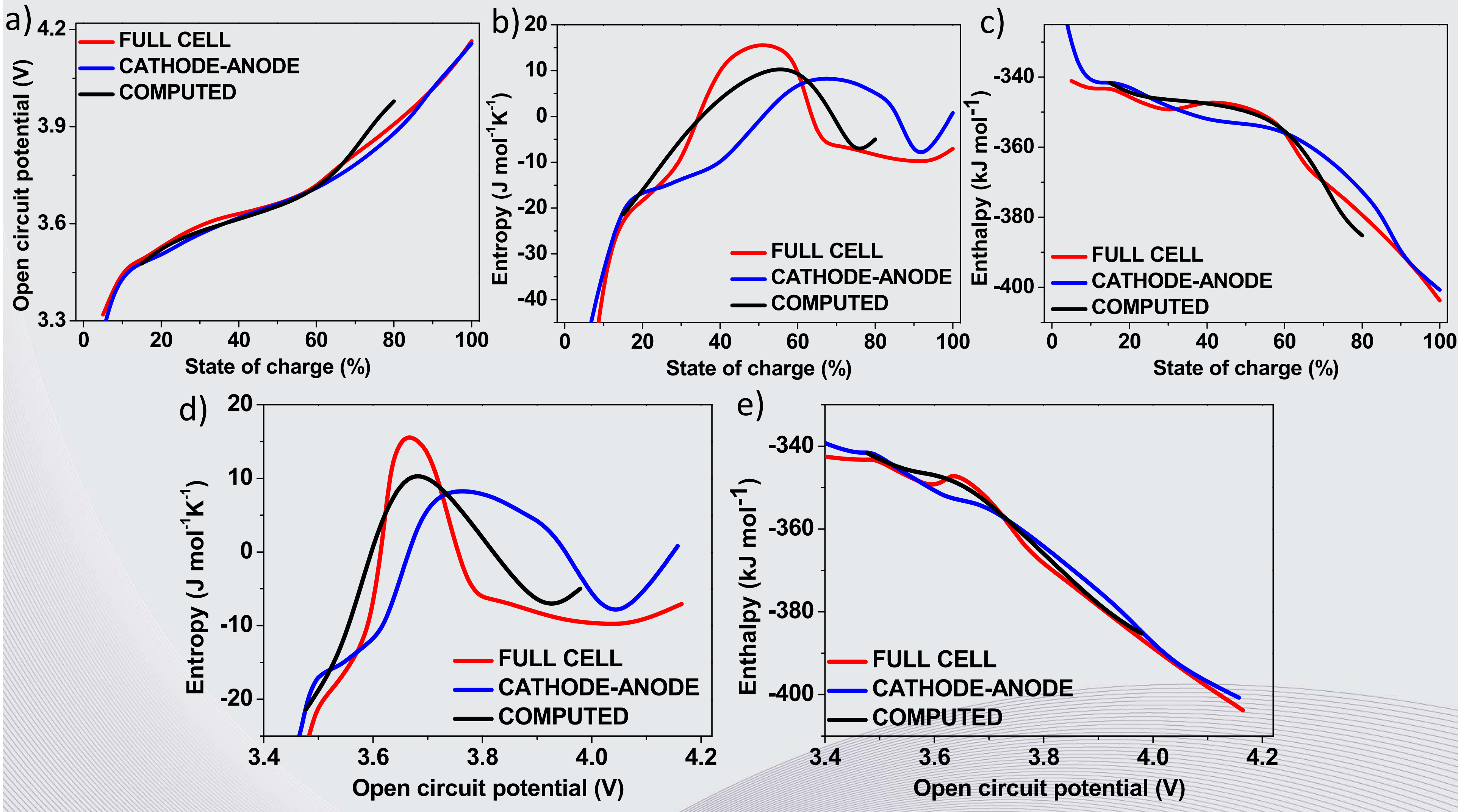
c)



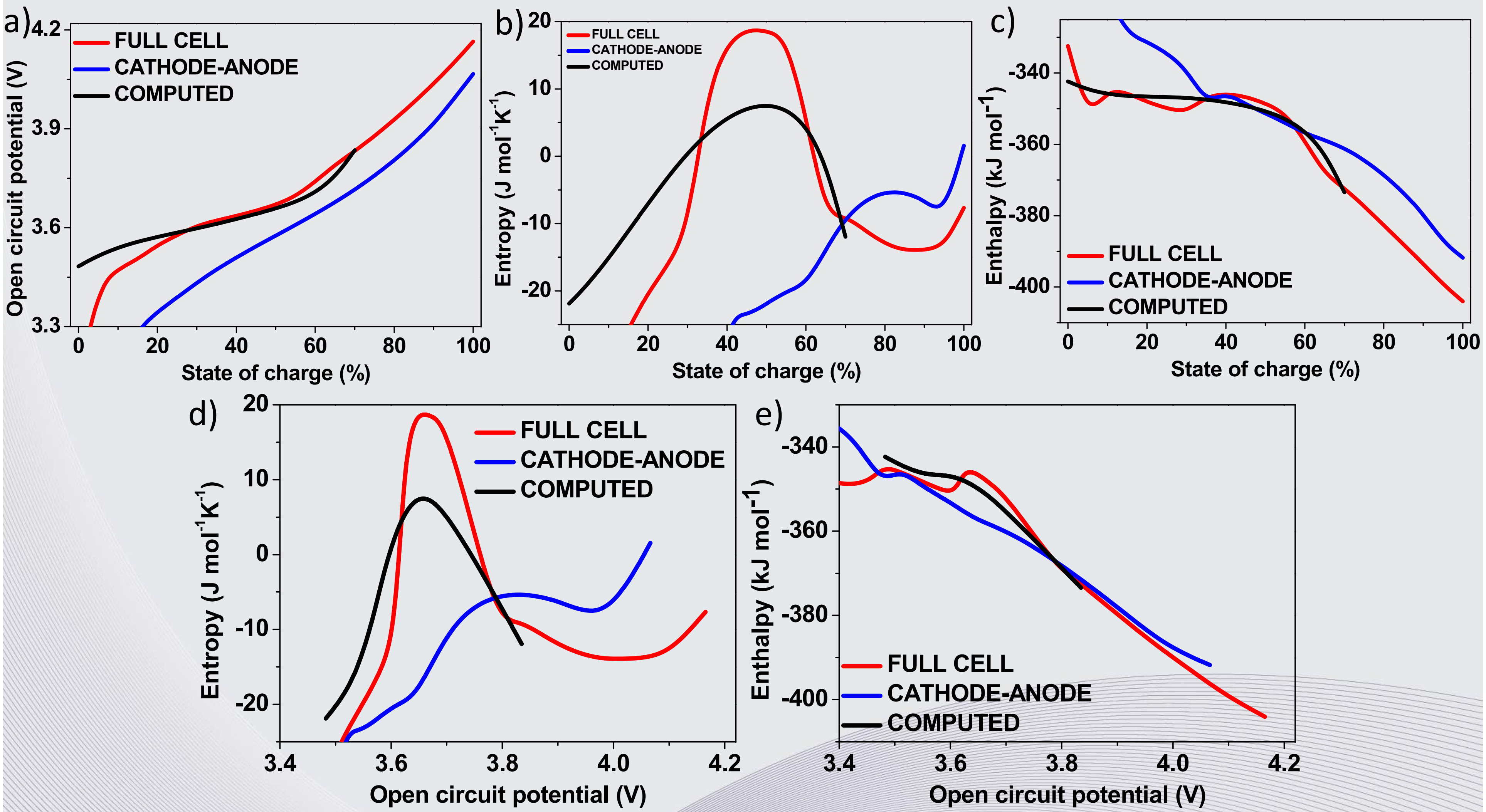
3. Enthalpy mismatch



Mismatch reduction by iterative computation



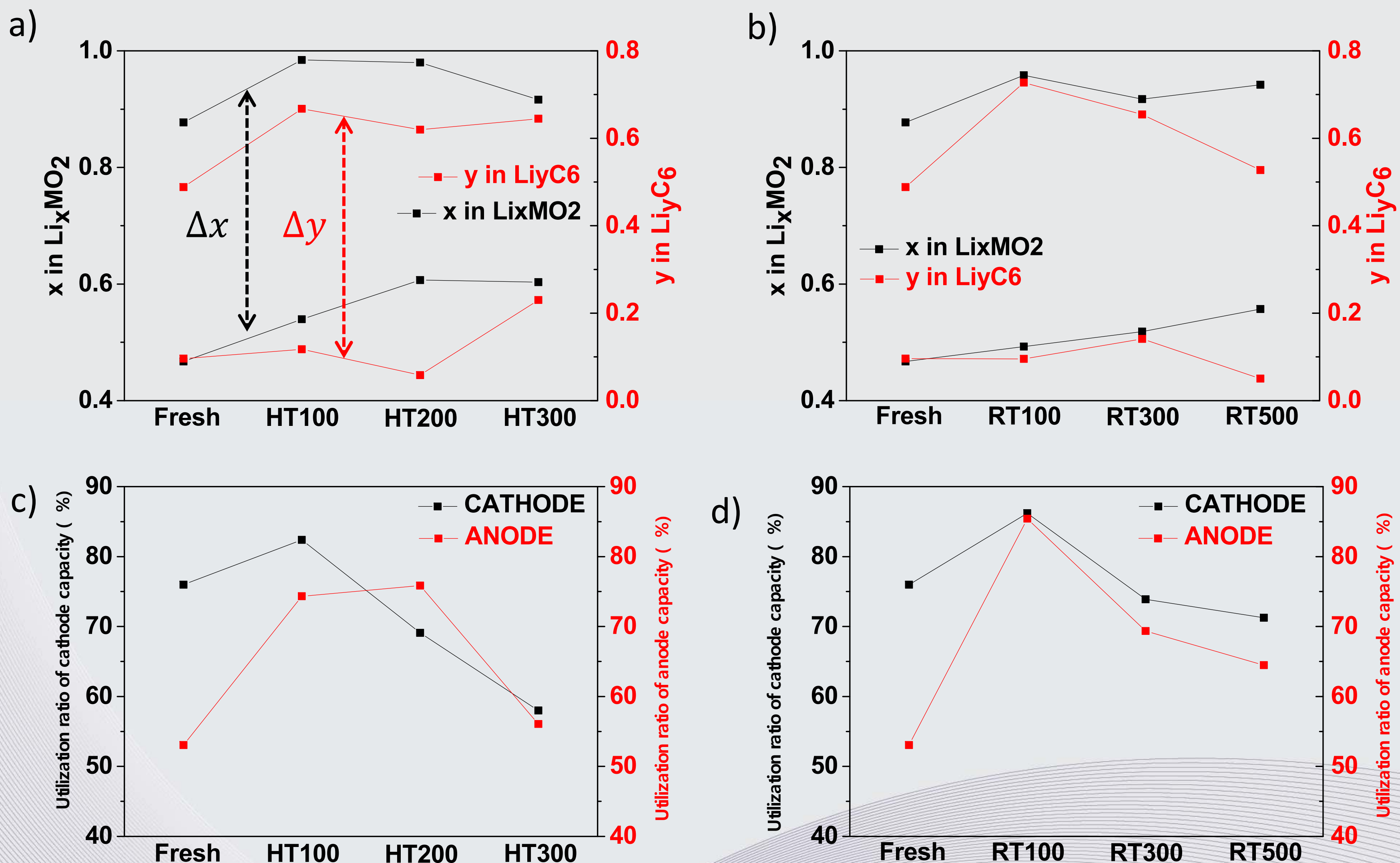
Mismatch reduction in aged cells (300#, 55 °C)



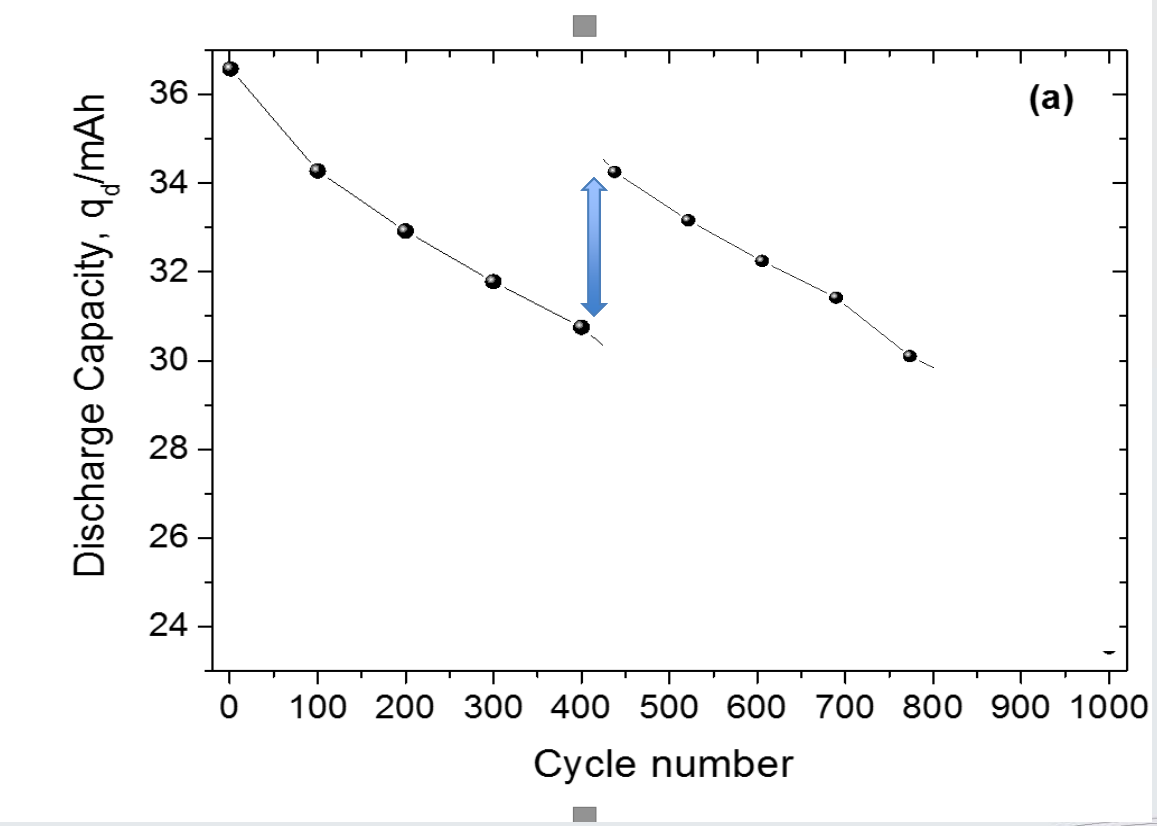
Computed parameters for fresh and aged cells

Sample		Fresh	HT100	HT200	HT300	RT100	RT300	RT500
Capacity (mAh/cm^2)	Cathode	2.28	2.11	1.94	1.99	2.31	2.28	2.18
	Anode	1.84	2.23	1.91	2.05	2.11	1.94	1.99
Fitting parameters	α_c	0.91	1.32	1.23	1.00	1.24	1.08	1.10
	β_c	9.49	-19.15	-19.80	1.17	-10.19	0.71	-6.25
	α_a	0.82	0.95	1.12	0.78	1.15	1.01	0.92
	β_a	-1.75	-14.96	-24.18	-20.86	-32.06	-29.18	-1.53
Calculated parameters	**a**	0.41	0.44	0.37	0.31	0.47	0.40	0.38
	b	0.88	0.98	0.98	0.92	0.96	0.92	0.94
	c	0.39	0.55	0.56	0.41	0.63	0.51	0.48
	d	0.10	0.12	0.06	0.23	0.10	0.14	0.05
Lithium composition range	x_{max}	0.88	0.98	0.98	0.92	0.96	0.92	0.94
	x_{min}	0.47	0.54	0.61	0.60	0.49	0.52	0.56
	y_{max}	0.49	0.67	0.62	0.64	0.73	0.65	0.53
	y_{min}	0.10	0.12	0.06	0.23	0.10	0.14	0.05

Lithium composition ranges in anode and cathode



Cell Regeneration



x_{max}	**0.92**
x_{min}	0.60
y_{max}	0.62
y_{min}	0.06

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Summary

- A new method for accurate assessment of lithium composition in anode and cathode has been developed for the first time

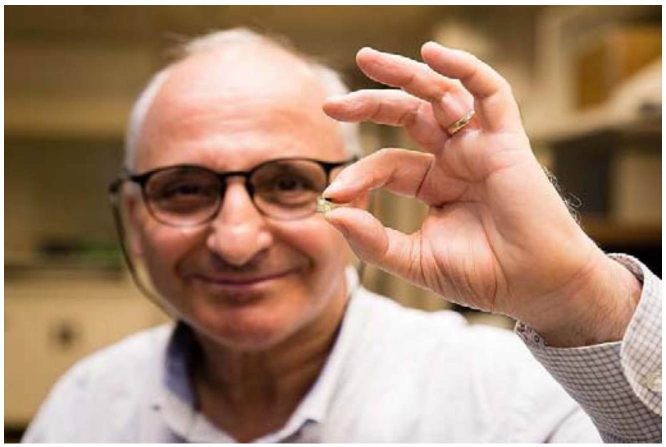
- The method is based on ETM + data computation to reduce mismatch between full-cell and half-cells data

- Anode and cathode were found to operate with a relatively low utilization rate ~50-75%

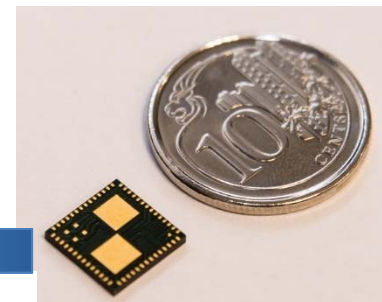
- The method can be used to improve battery performances during manufacturing

- Anode and cathode performance decay differently according to ageing conditions

The Smart CHIP



- One Chip for each fast charger



Artificial Intelligence Technology

Connected Objects
A Brain in Each Charger

Summary

- Entropymetry addresses major battery issues including
  - Chemistry, SOC, SOH and SOS
- Two ultra-fast charging methods have been developed:
  - NLV (natural charging in ~ 20 min)
  - CPC (possibly in ~10 min)
- These new methods are safe and allow for long cycle life (>1300#)


Thank you
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