ELECTROCHEMICAL LI-ION CELL MODELIZATION FOR ELECTRIC VEHICLES

ANDREA FALCONI

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Renaud CORNUT

Christine LEFROU

David SICSIC

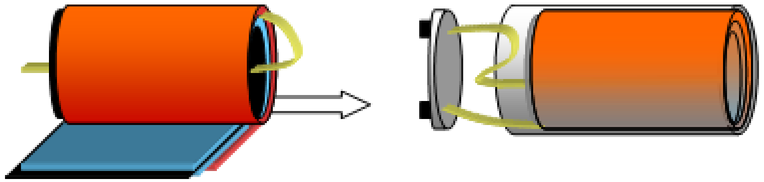
COMSOL CONFERENCE 2015 GRENOBLE

BATTERY PACK APROACHES

THE BATTERY PACK ASSIGNS THE ELECTRICAL VEHICLE'S PERFORMANCES

Sport car

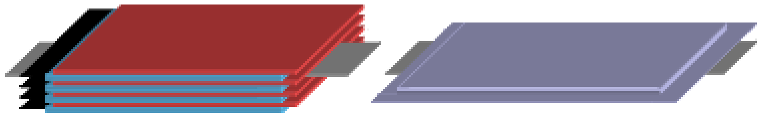
Long range - high cost - 450 kg



2.4 Ah / 45g – 190 Wh/kg

Family car

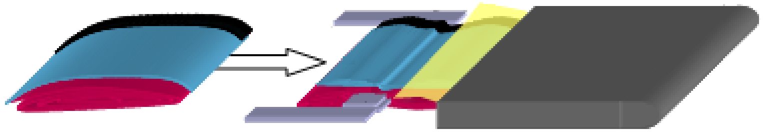
Mid range - moderate cost - 230 kg



32 Ah / 1kg – 130 Wh/kg

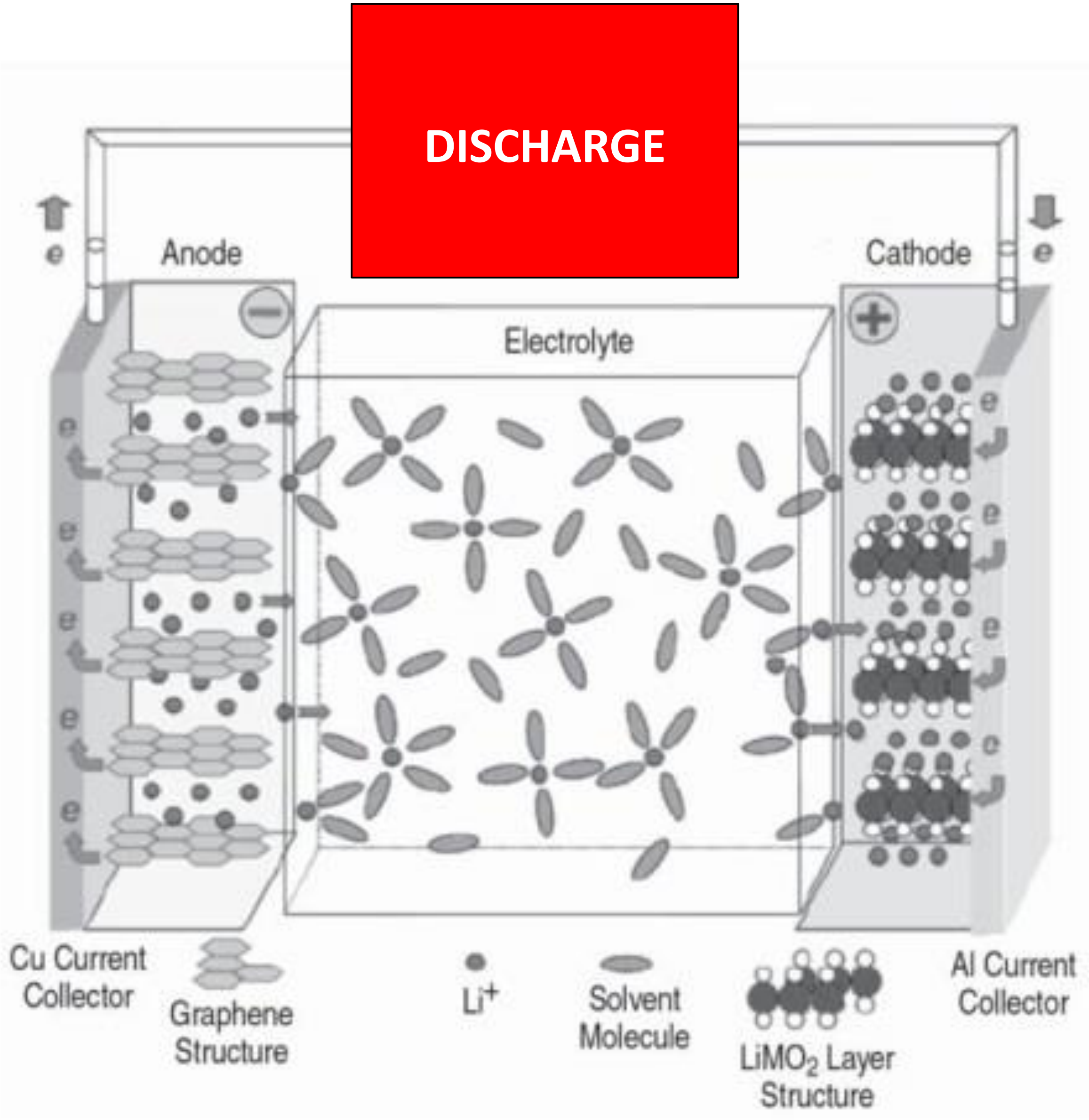
Urban car

Low range - low cost - 200 kg



50 Ah / 1.7 kg – 110 Wh/kg

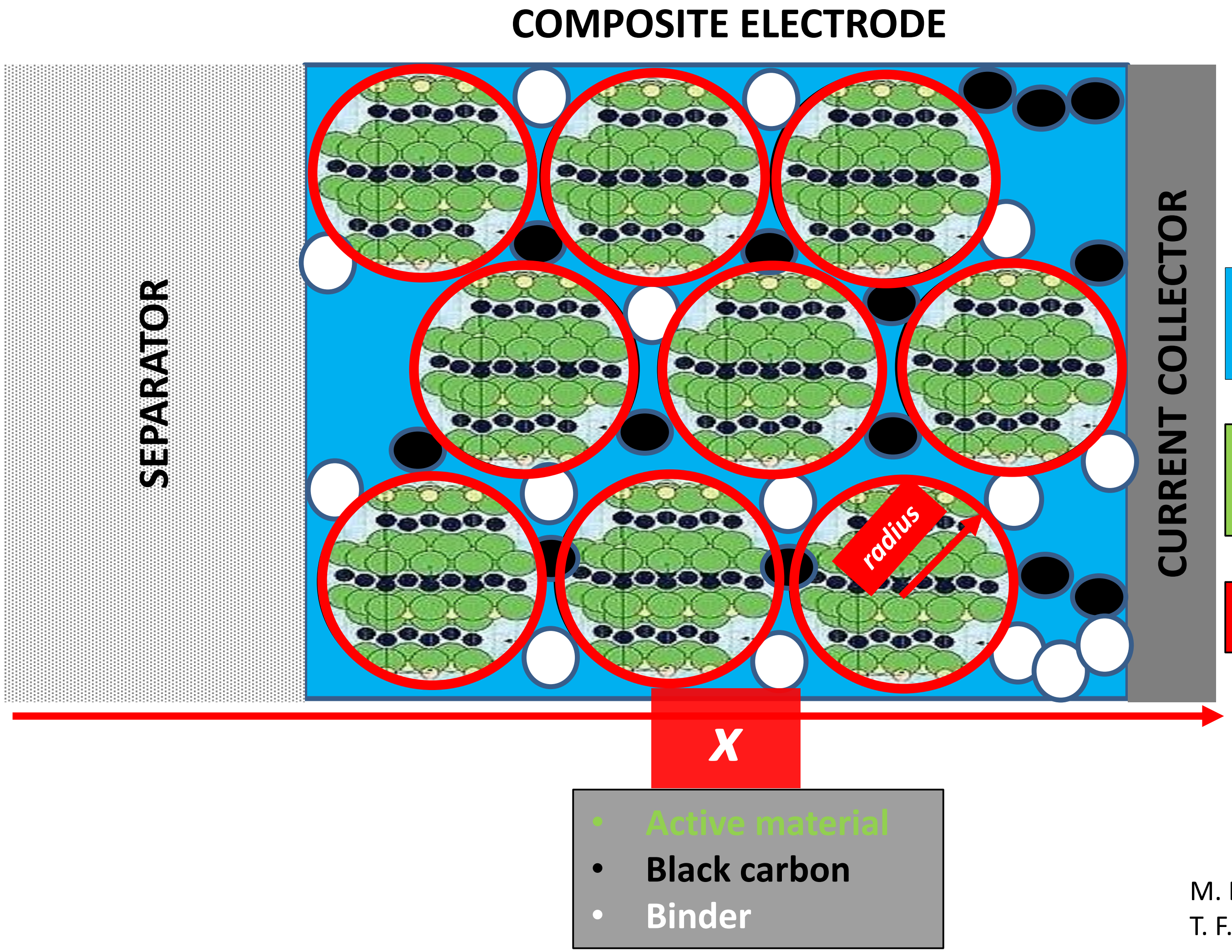
HOW DO LITHIUM-ION BATTERIES WORK?



INTERCALATION REACTION

- Negative : $C + xLi^{+} + xe^{-} \underset{charge}{\overset{discharge}{\rightleftarrows}} Li_{x}C$
- Positive : $LiMO_{2} \underset{charge}{\overset{discharge}{\rightleftarrows}} Li_{1-x}MO_{2} + xLi^{+} + xe^{-}$

POROUS THEORY BASED MODEL



- 12 EQUATIONS SOLVED WITH COMSOL
- 27 VOLUME AVERAGED PARAMETERS

- *Liquid phase ideal mass transport (migration + diffusion)*
- *Liquid phase potential (ionic Ohm law)*

- *Solid phase diffusion*
- *Solid phase potential (electronic Ohm law)*

- *Li+/Li charge transfer (Insertion reaction kinetics)*

M. Doyle, et. al., J. Electrochem. Soc. 140 (1993) 1526
T. F. Fuller, M. Doyle and J. Newman, *J. Electrochem. Soc.*, 141 (1994)

NON DIMENSIONAL EQUATIONS

Adimensionnalization

- Parameters from 27 to 16
- Generalize the simulation results
- Highlight some parameters connections
- Identification of the system time constants

Dimensionless	
$\tilde{t} = t \dfrac{1}{\varepsilon_{+l}} \dfrac{D_{e+}}{d_+^2}$	Time
$\tilde{j} = j \dfrac{d_+}{D_{e+}\, F\, C^*}$	Current
$\tilde{\varphi} = \dfrac{F}{RT} \varphi$	Voltage
$\tilde{x} = \dfrac{x}{d_{+-e}}$	Thickness

- $\tilde{t} = \dfrac{t}{89\,[s]}$
- $\tilde{j} = \dfrac{j}{14.3[Am^{-2}]}$
- $\tilde{\varphi} = \dfrac{\varphi}{25[mV]}$
- $\tilde{x} = \dfrac{x}{60[\mu m]}$

CLASSIC DISCHARGE @ 1C-rate*:

$\tilde{j} \cong 2$

$\tilde{t}_{100\,\%\,SOC} \cong 40$

Derived	
$A_{1\pm} = \dfrac{RT}{F} \dfrac{\sigma_\pm}{D_{e\pm}\, F\, C^*}$	Electronic conduction vs Li diffusion in the electrolyte
$A_{2\pm} = \varepsilon_{\pm s} \dfrac{D_{s\pm}}{D_{e\pm}} \dfrac{C_{s,max\pm}}{C^*} \left(\dfrac{d_\pm}{R_{p\pm}}\right)^2$	Solid phase diffusion vs Li diffusion in the electrolyte

*VALUES FROM LITERATURE:

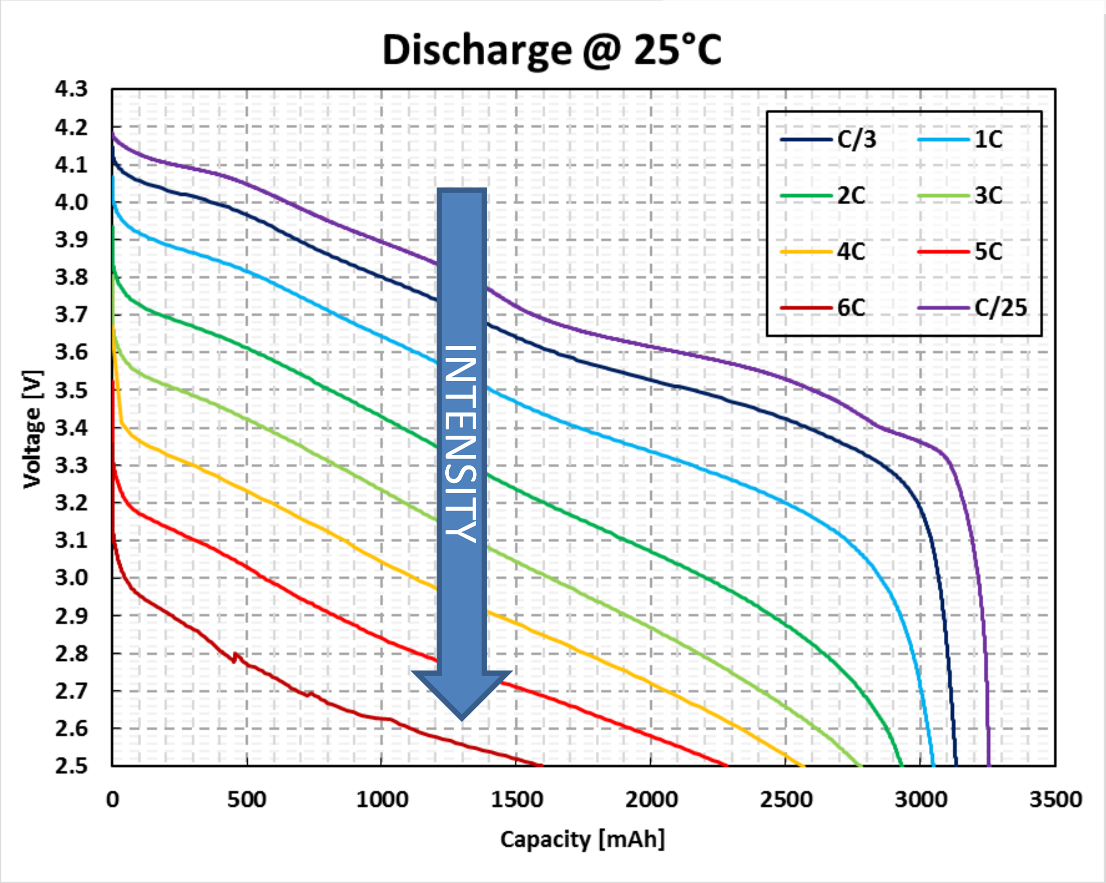
L. Zhang et al., Energies 2014, *7*, 6282-6305

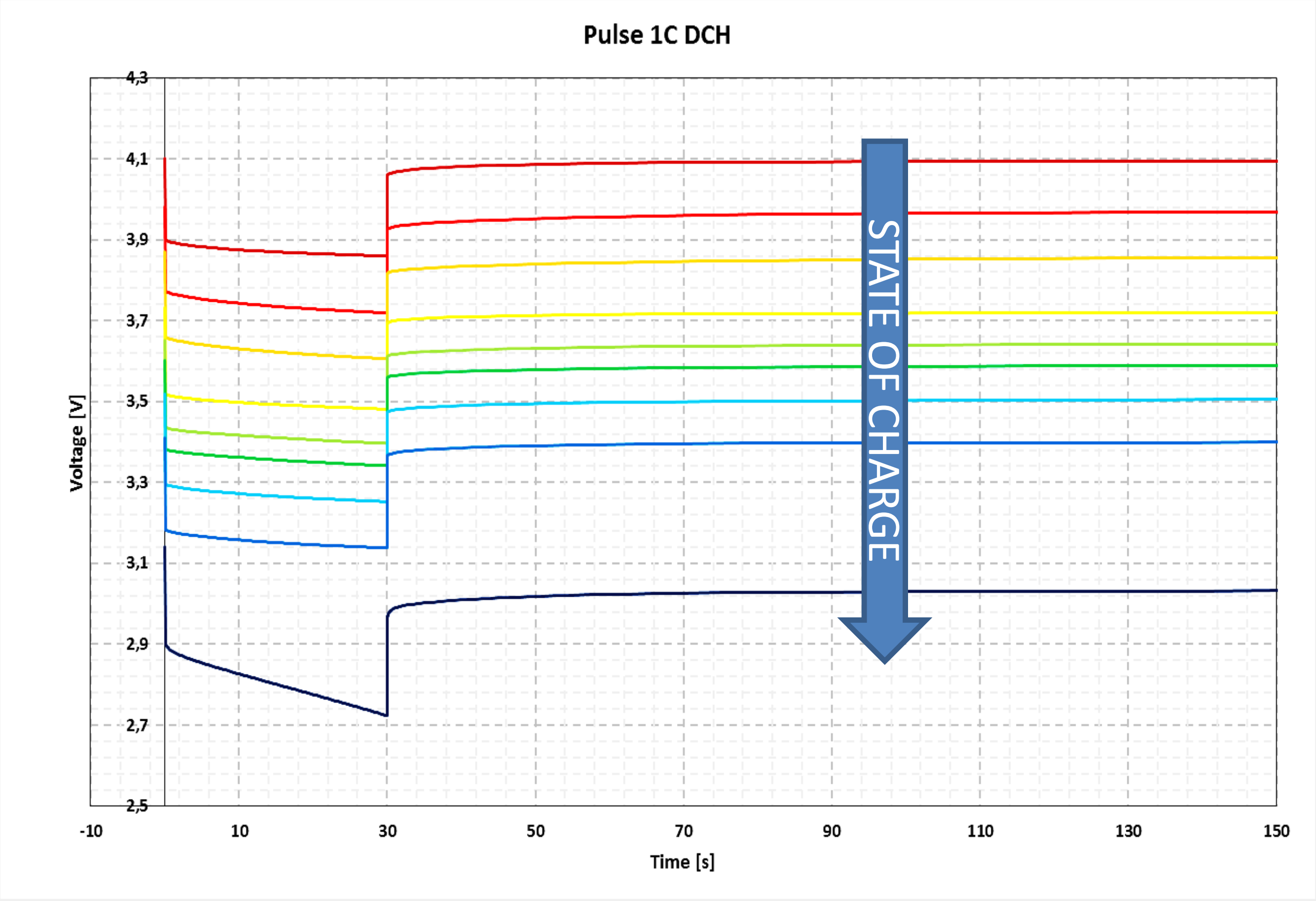
L. Valøena *et al.,* J. Electrochem. Soc. 152 (5) A882-A891 (2005)

EXPERITIMENTAL RESULTS ON HIGH ENERGY DENSITY CELL

COMMERCIAL CELL CHARACTERIZATION

- PREDICT THE PRACTICAL CAPACITY ;
- IDENTIFY IMPULSIONS AND RELAXATION PHENOMENA



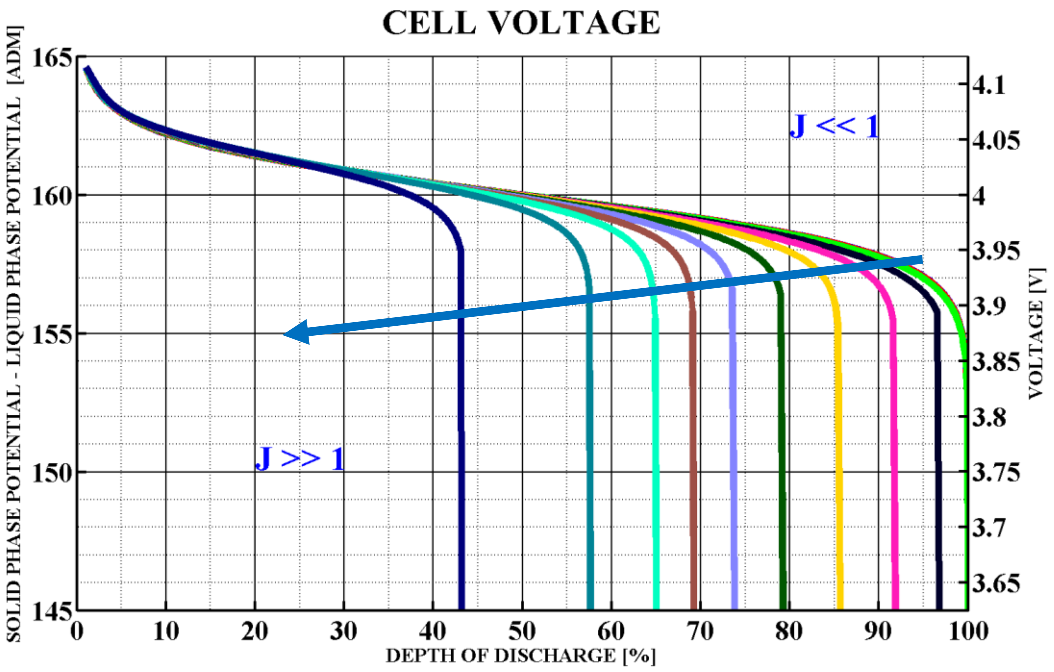


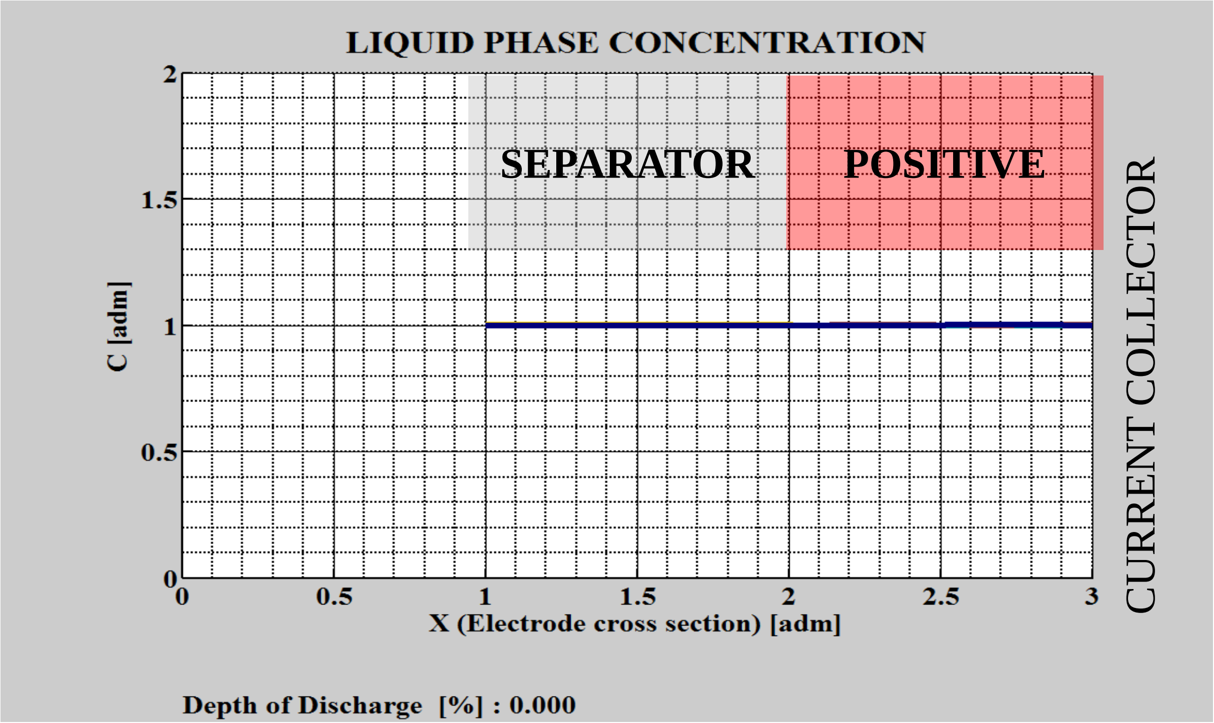
- SMOOTH END OF DISCHARGE DUE TO CUT OFF VOLTAGE.

GALVANOSTATIC DISCHARGE SIMULATION : VARIABLE CURRENT DENSITY

CONFIGURATION

- $A_{1\pm} = \frac{RT}{F} \frac{\sigma_\pm}{D_{e\pm} F C^*}$ (High Electronic Conductivity)
- $A_{2\pm} = \varepsilon_{\pm s} \frac{D_{s\pm}}{D_{e\pm}} \frac{C_{s,max\pm}}{C^*} \left(\frac{d_\pm}{R_{p\pm}}\right)^2$ (High Solid Diffusivity)



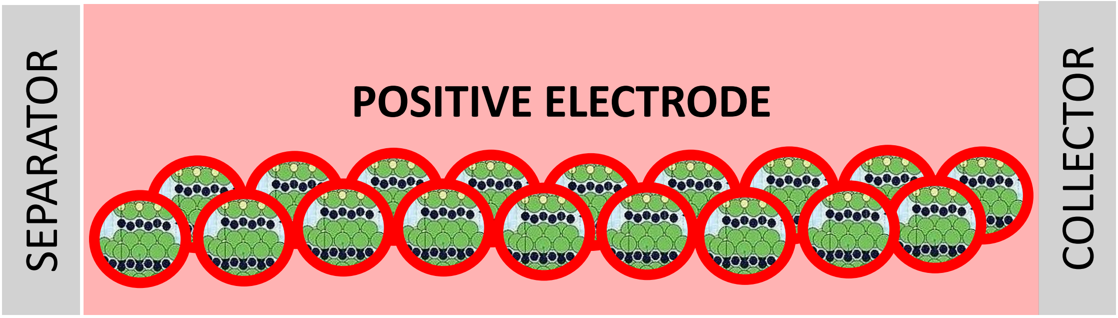


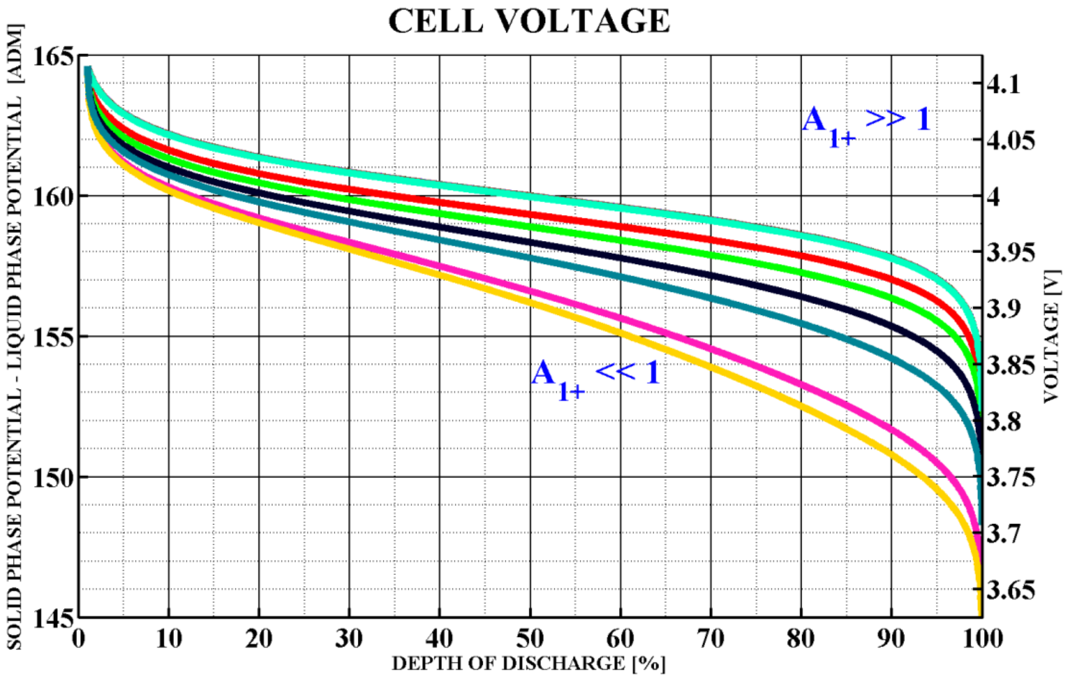
- DISCHARGE LIMITATION DUE TO LI+ DEPLETION

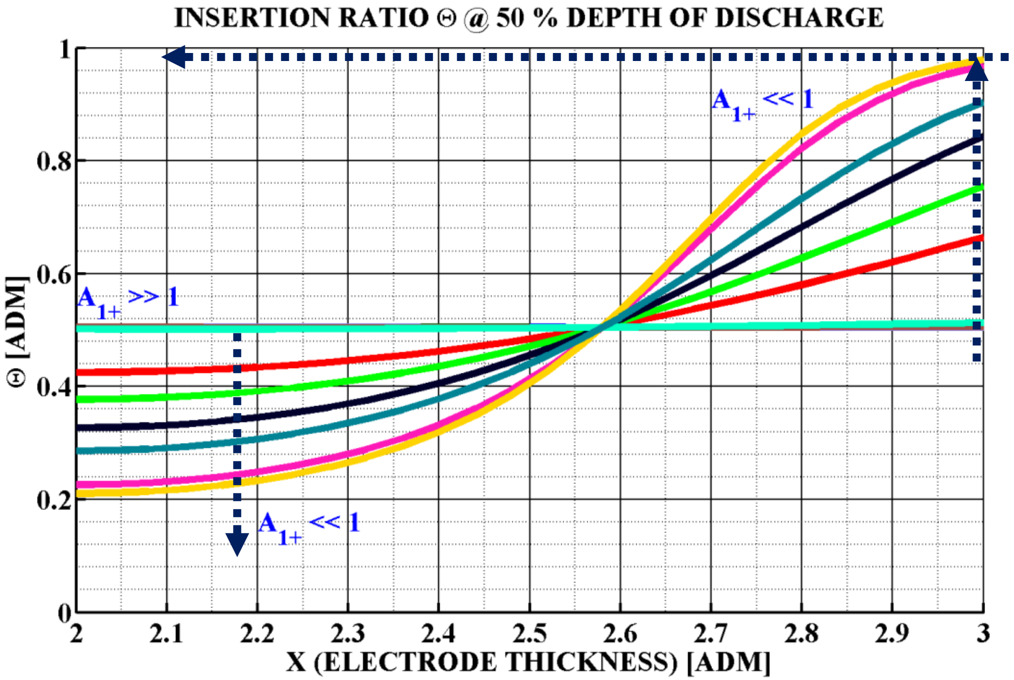
GALVANOSTATIC DISCHARGE SIMULATION : VARIABLE CONDUCTIVITY

CONFIGURATION :
- High Solid Diffusivity
- Variable electronic conductivity ;
- J << 1 (Constant Li+ concentration in the electrolyte)

$$A_{1\pm} = \frac{RT}{F} \frac{\sigma_{\pm}}{D_{e\pm}\, F\, C^{*}}$$





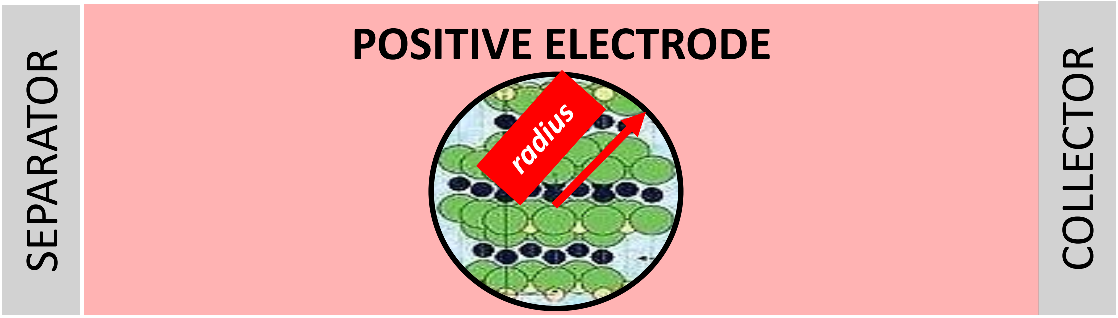


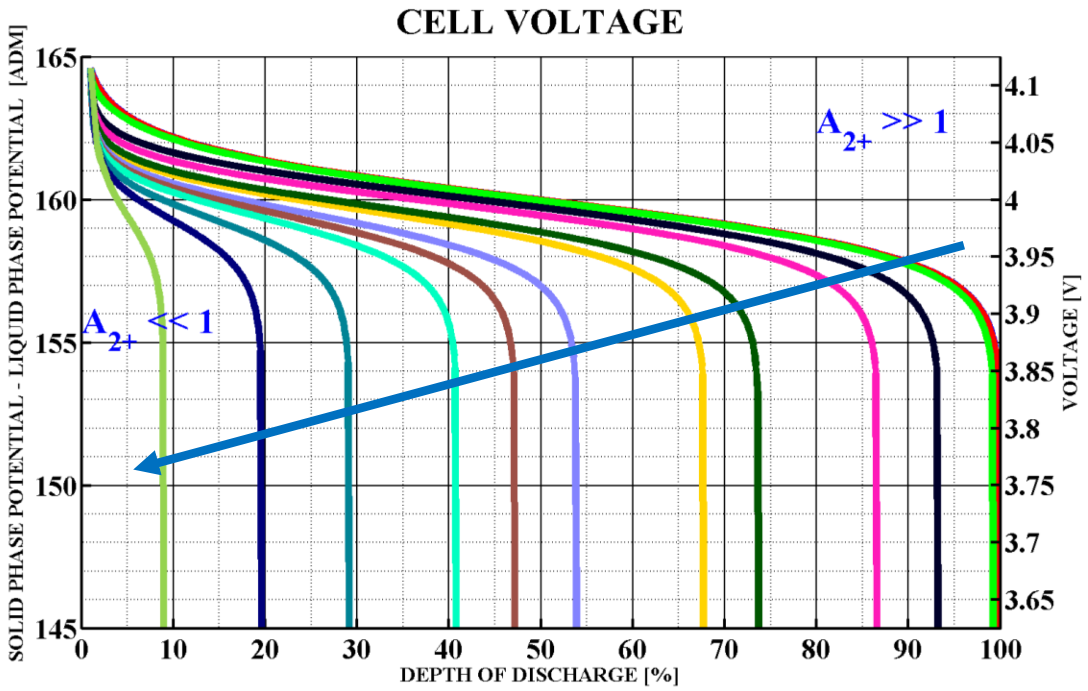
- POLARIZATION DUE TO SOLID PHASE CONCENTRATION
- THE INSERTION RATIO @ 50 % IS HIGHER AT COLLECTOR AND LOWE NEAR THE SEPARATOR BECAUSE THE ELECTRONS MINIMIZE THE PATH;

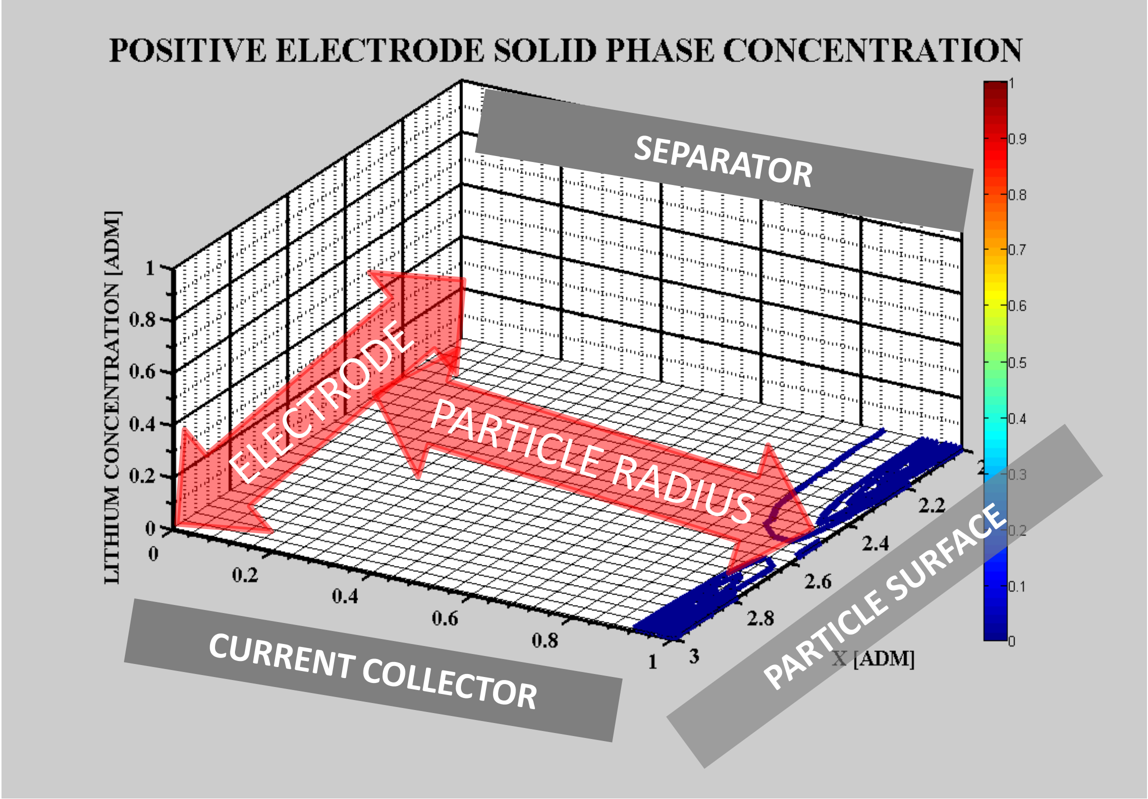
GALVANOSTATIC DISCHARGE SIMULATION : VARIABLE DIFFUSIVITY

CONFIGURATION :
- High Conductivity
- Variable solid phase diffusitvity
- J << 1 (Constant Li+ concentration in the electrolyte)

$$A_{2\pm} = \varepsilon_{\pm s} \frac{D_{s\pm}}{D_{e\pm}} \frac{C_{s,max\pm}}{C^*} \left(\frac{d_\pm}{R_{p\pm}}\right)^2$$





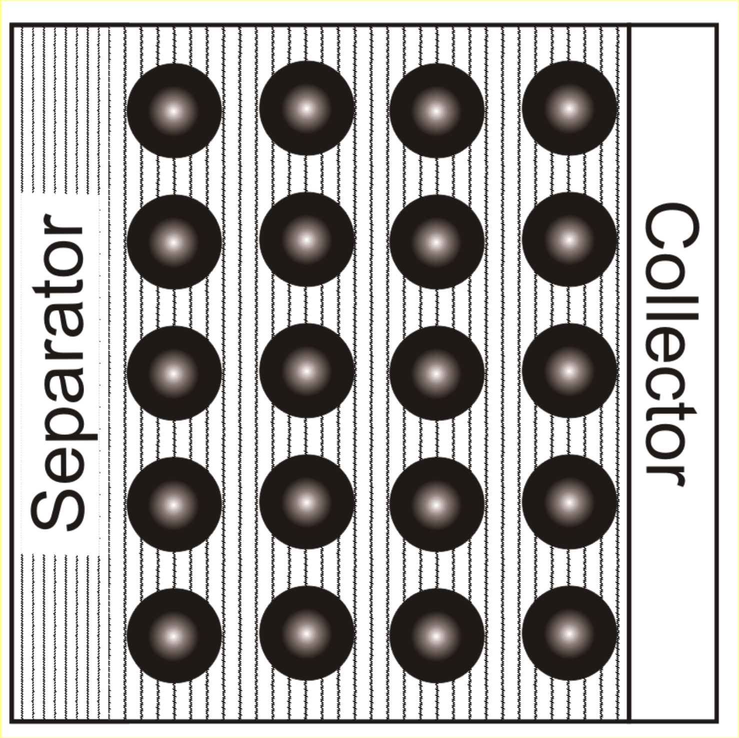


- WHEN THE EXTERNAL CONCENTRATION REACHES 1 FOR ALL THE PARTICLES THE DISCHARGE IS OVER;

DISCHARGE INTERRUPTION PHENOMENA RESUMED

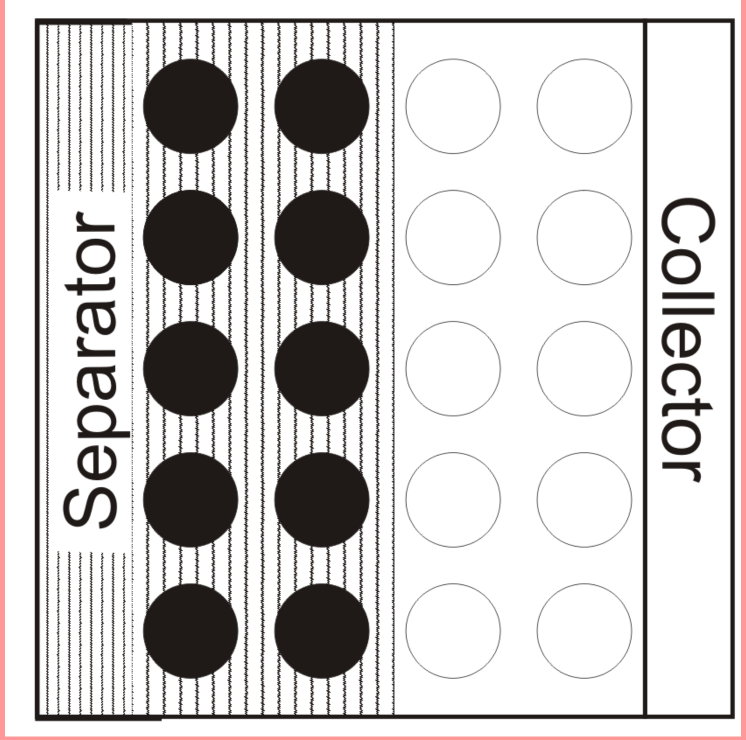
Solid Phase Diffusion

Lithium accumulation at particles surface



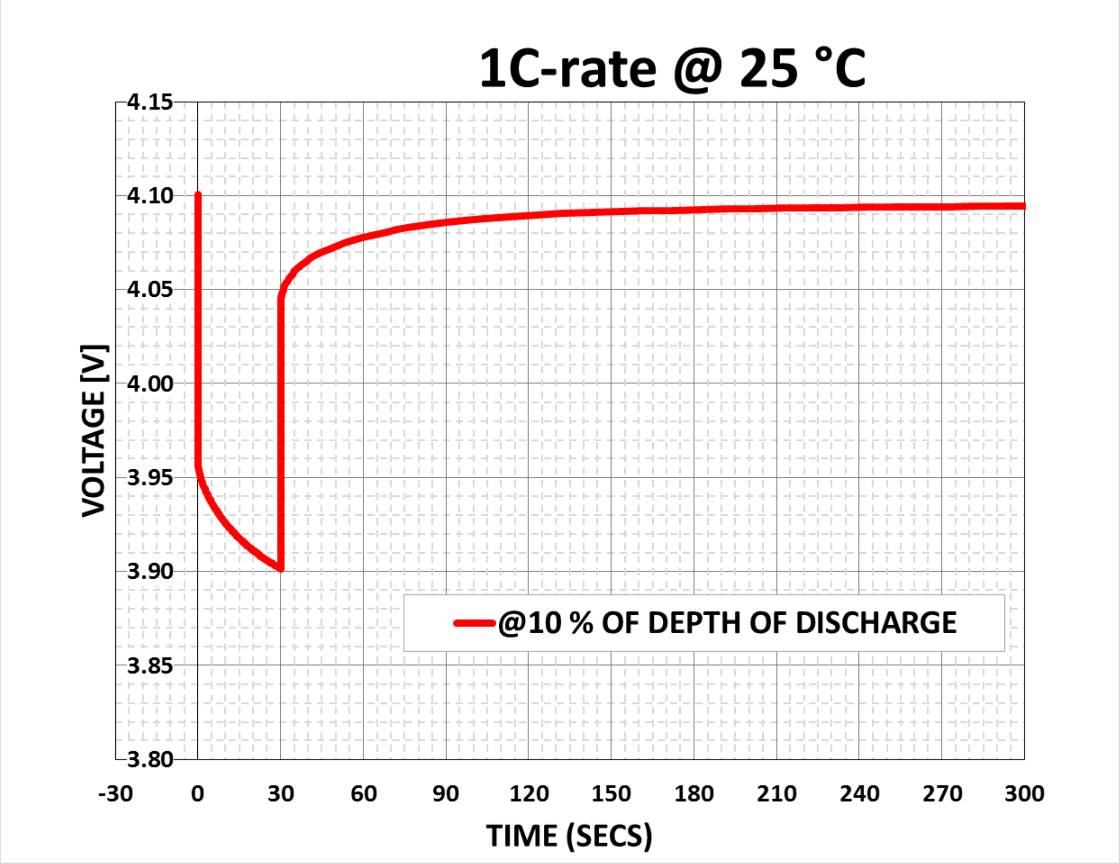
Liquid Phase Diffusion

Lithium depletion in the electrolyte



DIRECT CURRENT RESISTANCE

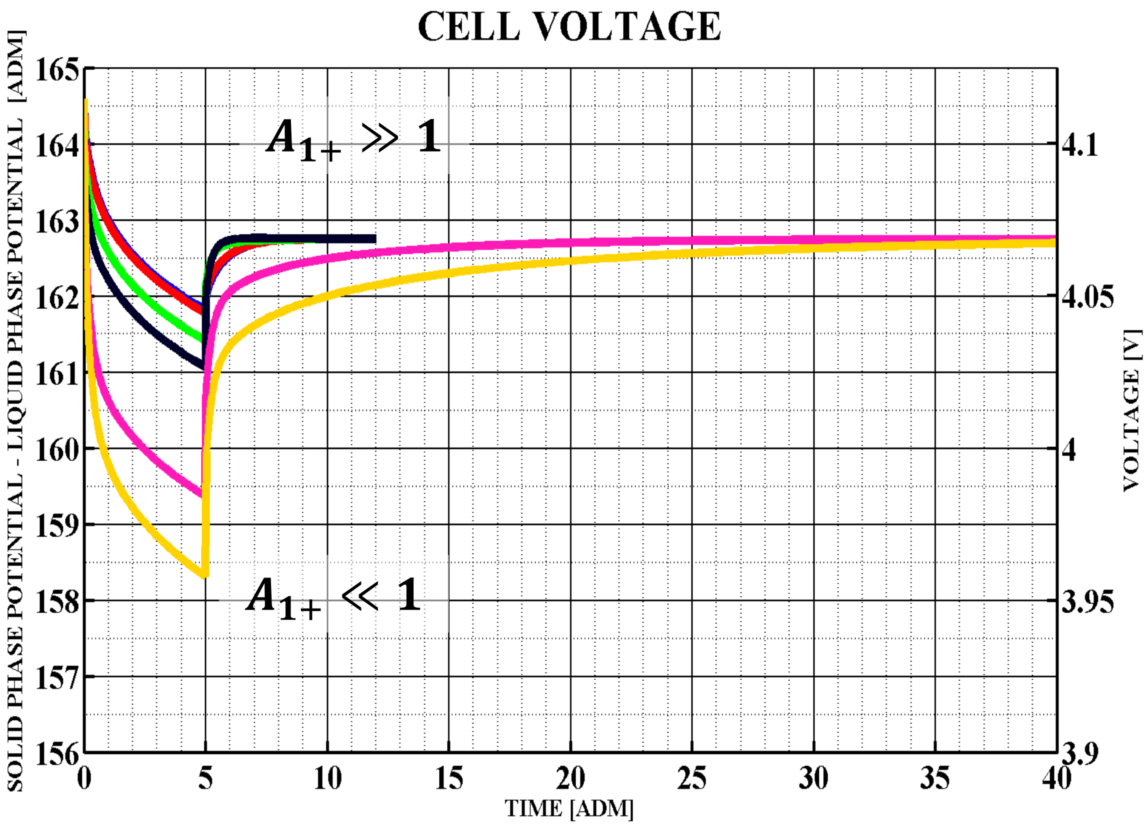
EXPERIMENTAL



SIMULATION

- Variable electronic conductivity
- J = 1

$$A_{1\pm} = \frac{RT}{F}\frac{\sigma_{\pm}}{D_{e\pm}\,F\,C^{*}}$$



- THE VOLTAGE PROFILE IS REPRODUCED WITH THE RELAXATION
- THE SOME PARAMETERS COULD BE IDENTIFIED WITH PULSES AND RELAXATIONS

CONCLUSIONS

- Dimensionless simulation of Lithium ion cell discharge with COMSOL coefficient form pde.
- Identify different limiting discharge phenomena and reduction of parameters.

SHORT TERM PERSPECTIVES

- Find other limiting factors and conditions.
- Create specific tests for the parameters tuning.

THANK YOU FOR YOUR ATTENTION. QUESTIONS ?