



The 27th INTERNATIONAL
ELECTRIC VEHICLE
SYMPOSIUM & EXHIBITION
BARCELONA
17th-20th November 2013

**Fast Charging Method
Based on Estimation of Ion Concentrations
using
a Reduced Order of Electrochemical Thermal Model for Lithium
Ion Polymer Battery**

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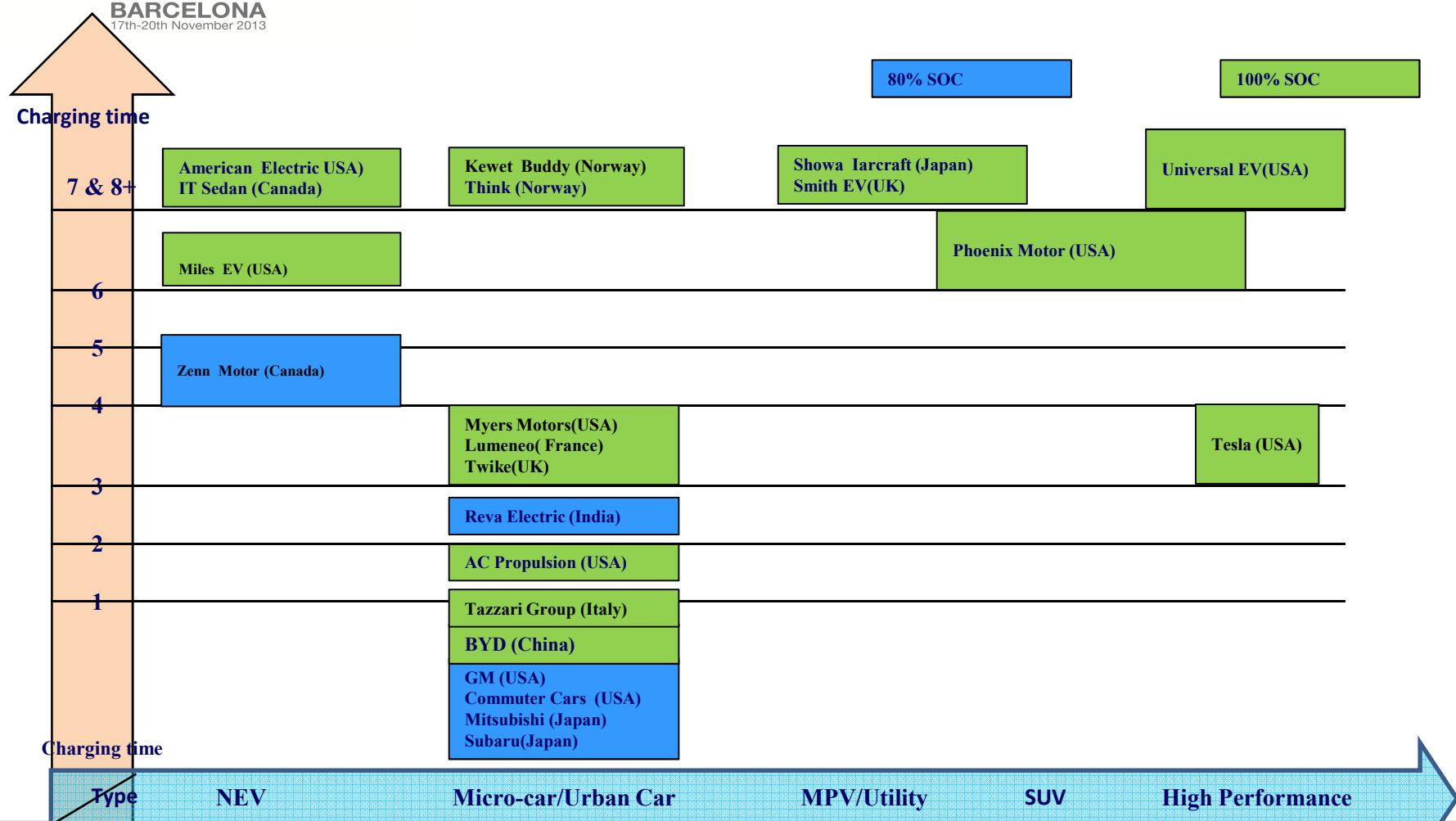
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Background: Charging time of BEVs



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1 or 2-Step CC + CV
charging

Multi-Step CC Charging

Multi-Step CC Charging +
Taper Charging

- CC(Constant Current)
- CV (Constant Voltage)
- Taper Charging
- Constant Power Charging

Pulse Charging

- One-Directional Pulse
- Bi-Directional Pulse

Optimization for reduction of charging time, battery life or efficiency

1. **Experimental data:** Ant-Cycle System, Wolf Pack , Taguchi-based Algorithm, Sinusoidal Current Charging with the Minimum AC Impedance, Grey Prediction Technique
2. **Control theory and model:**
 - Fuzzy Controls, Residual Energy Evaluation, Built-in Resistance Compensator , Multiple Rate, Probabilistic Fuzzy Neural Network Control, integral linear programming algorithm, first order dynamic model, a single one-step prediction
3. **Cycle numbers or SOC**
 - Offline battery charger, Negative Pulse Discharge, Frequency- varied Technique

Proposed methods do not consider fundamental transport mechanism of lithium ions and their intercalation/de-intercalation in details

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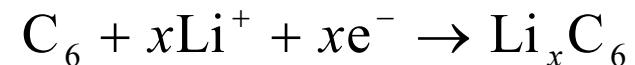


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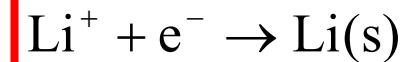


Limiting factors for high current Charging

- The reaction on the negative electrode is described as:



- When operated improperly, Li-ions are deposited on the anode surface instead of intercalating during charging:



Causes of Lithium plating:

- ✓ Large current rate during charging, especially at high Li ion concentration
- ✓ Low temperature

Effects of Lithium plating:

- ✓ Capacity
 - Irreversible loss of active Lithium
- ✓ Safety
 - Dendrites can cause shorts within the electrodes
- ✓ Heat generation
 - A mat of dead lithium and dendrites can increase the chances minor shorts will lead to thermal runaway



Reference: C. J. Mikolajczak, J. Harmon, *From Lithium plating to Lithium-ion cell runaway* Exponent [E^x(40)] annual report, 2009

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Models for Estimation ion concentrations

High

Improvement of cell
designs

**Full order of Electrochemical, thermal and
mechanical Model (ETMM: FOM):**

Electrochemical kinetics, Potential theory,
energy and mass balance, and charge
conservation , Ohm's law, Empirical OCV and
elasticity

Intermediate

BMS Functionalities

**Reduced order of Electrochemical thermal
Model (ETM: ROM):** Empirical OCV

Polynomial, State space, Páde approx., POD,
Galerkin Reformulation and others

Low

Electric equivalent circuit Model (EECM):
Randles models with the 1st, 2nd and 3rd
order

Comp. time

Accuracy

Fira Barcelona



Low

Moderate

High

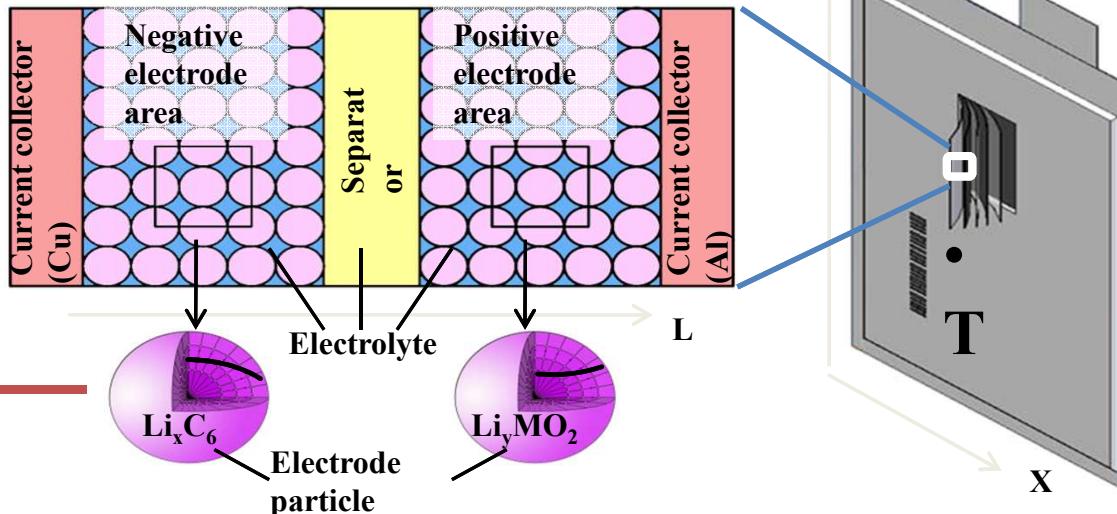
AVERE weA



EVAP EDTA

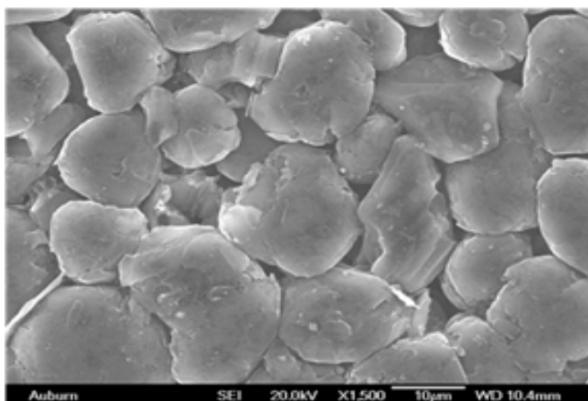


- c_e
- Φ_e
- Φ_s
- η_{SEI}
- c_s

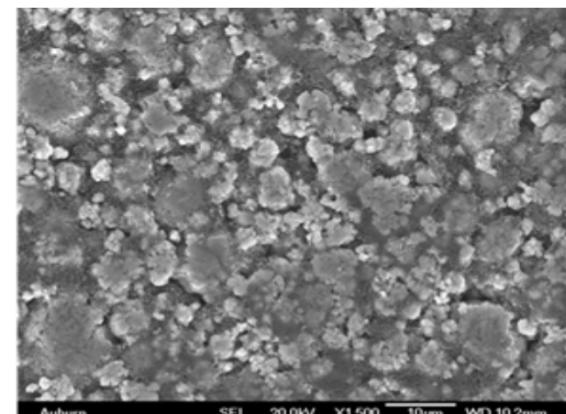


Cell specification	
Anode	Carbon
Cathode	$Li[MnNiCo]O_2$ (NMC),
Separator	polymer
Electrolyte	$LiPF_6$, EC/DMC
Size	164mm×250m m×5mm
Capacity	15.7Ah

SEM
(anode side)



SEM
(cathode side)



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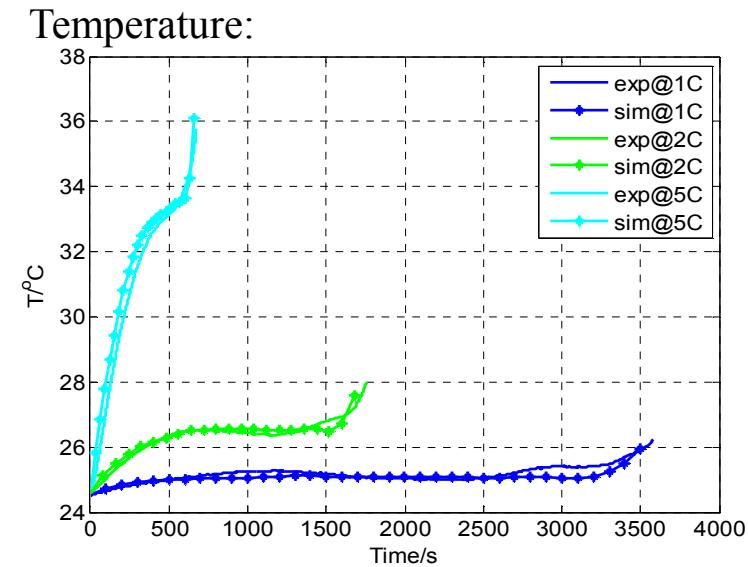
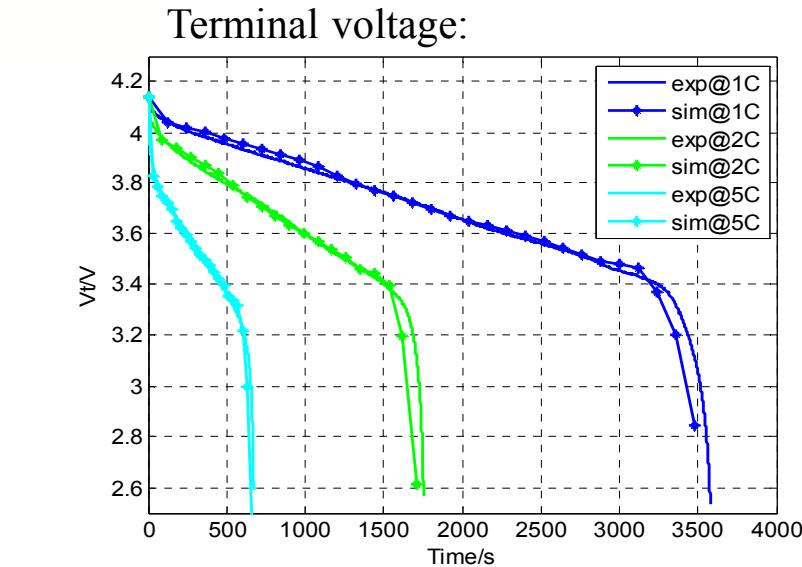


Models based on electrochemical and thermal principle

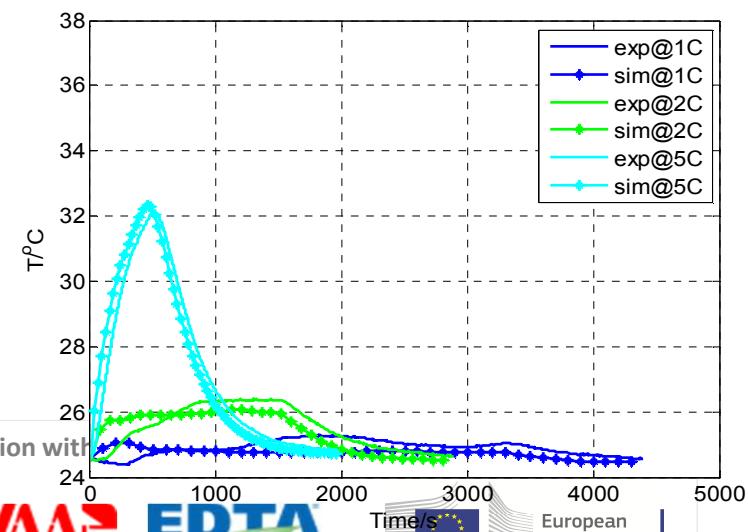
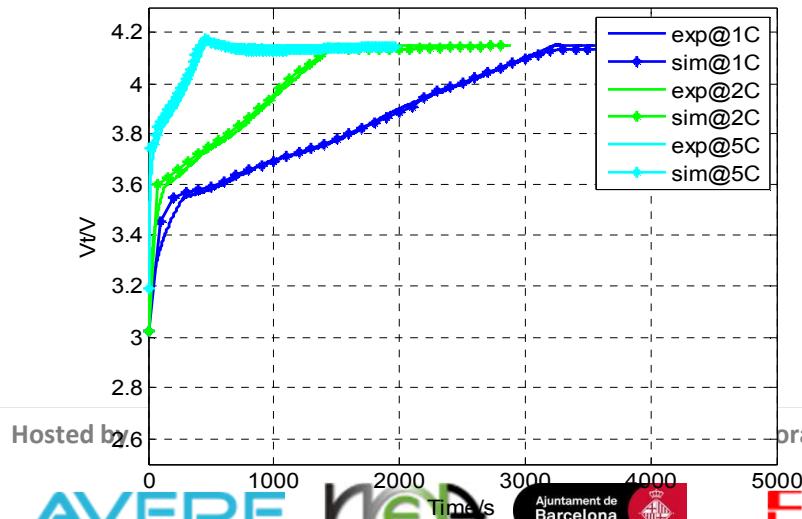
	Full Order Model (FOM)	Reduced Order Model(ROM)	Order reduction
Ion concentration in solid particles $C_s \rightarrow$ Polynomial approach	$\frac{\partial C_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_s}{\partial r} \right)$	$\frac{d}{dt} C_{s,ave} + 3 \frac{j^{Li}}{R_s a_s F} = 0$ $\frac{d}{dt} q_{ave} + 30 \frac{D_s}{R_s^2} q_{ave} + \frac{45}{2} \frac{j^{Li}}{R_s^2 a_s F} = 0$ $35 \frac{D_s}{R_s} (C_{s,surf} - C_{s,ave}) - 8 D_s q_{ave} = - \frac{j^{Li}}{a_s F}$	$N_R * N_L$ to $3 * N_L$
Ion concentration in electrolyte $C_e \rightarrow$ State space approach	$\dot{\mathbf{c}}_e = \mathbf{A} \cdot \mathbf{c}_e + \mathbf{B} \cdot I$ $\mathbf{y} = \mathbf{C} \cdot \mathbf{c}_e + \mathbf{D} \cdot I$	$\dot{\mathbf{c}}_e = \mathbf{A}^* \cdot \mathbf{c}_e + \mathbf{B}^* \cdot I$ $\mathbf{y} = \mathbf{C}^* \cdot \mathbf{c}_e + \mathbf{D}^* \cdot I$	N_L to 3
Potentials and current density \rightarrow Parameters simplification	$\frac{\partial}{\partial x} \left(\sigma^{eff} \frac{\partial}{\partial x} \phi_s \right) - j^{Li} = 0$ $\frac{\partial}{\partial x} \left(k^{eff} \frac{\partial}{\partial x} \phi_e \right) + \frac{\partial}{\partial x} \left(k_D^{eff} \frac{\partial}{\partial x} \ln c_e \right) + j^{Li} = 0$ $j^{Li} = a_s i_0 \left\{ \exp \left[\frac{\alpha_a F}{RT} \eta \right] - \exp \left[- \frac{\alpha_c F}{RT} \eta \right] \right\}$	$\frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} \phi_{se} \right) = j^{Li} \left(\frac{1}{\sigma^{eff}} + \frac{1}{k^{eff}} \right)$ $j^{Li} = \frac{a_s i_0 F}{RT} (\phi_{se} - U)$	$2 * N_L$ to $1 * N_L$
Energy equation and temperature dependence	$Q_{gen.} = \frac{1}{L} \int_L (\Delta U_{equ}^+ \cdot i(r, l) - \Delta U_{equ}^- \cdot i(r, l)) dl + \frac{I}{V} (U_{ocv} - V_T - T \cdot \frac{\partial U_{ocv}}{\partial T})$ $D_s = D_{s0} \cdot \exp \left(\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right)$		
SOC estimation	$SOC = \left[\frac{1}{L_-} \int_0^{L_-} \frac{(C_{s,ave} - C_{s,max} \cdot x_0)}{C_{s,max} \cdot (x_{100} - x_0)} \cdot dx \right] \cdot 100 \%$		



Test condition:
Mode: Depleting
Temperature: 25°C
Current: 1C, 2C, 5C
Initial SOC: 100%



Test condition:
Mode: Depleting
Temperature: 25°C
Current: 1C, 2C, 5C
Initial SOC: 0%



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AVERE

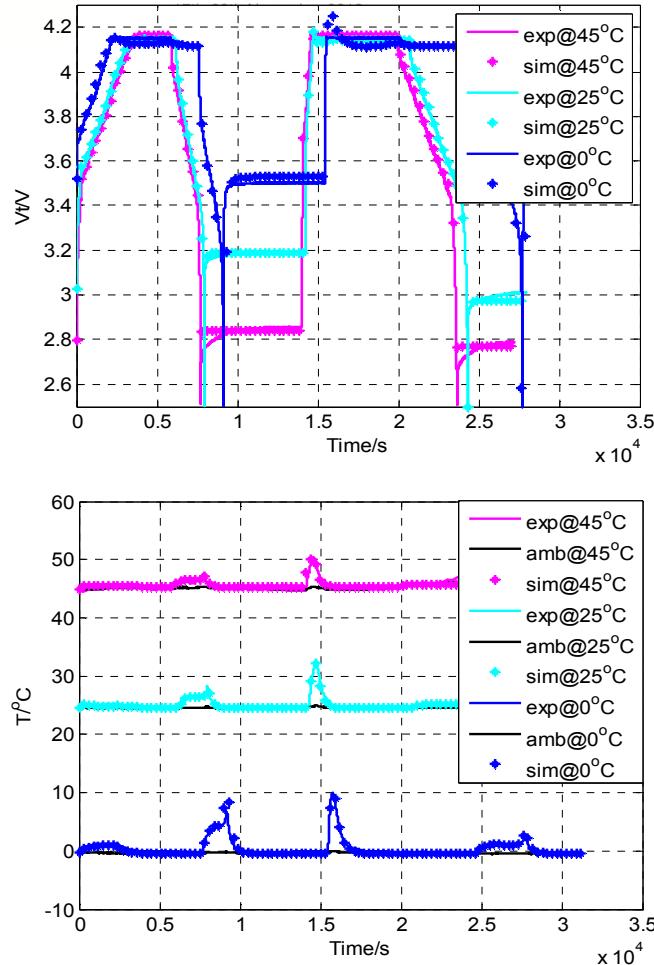


EVAA

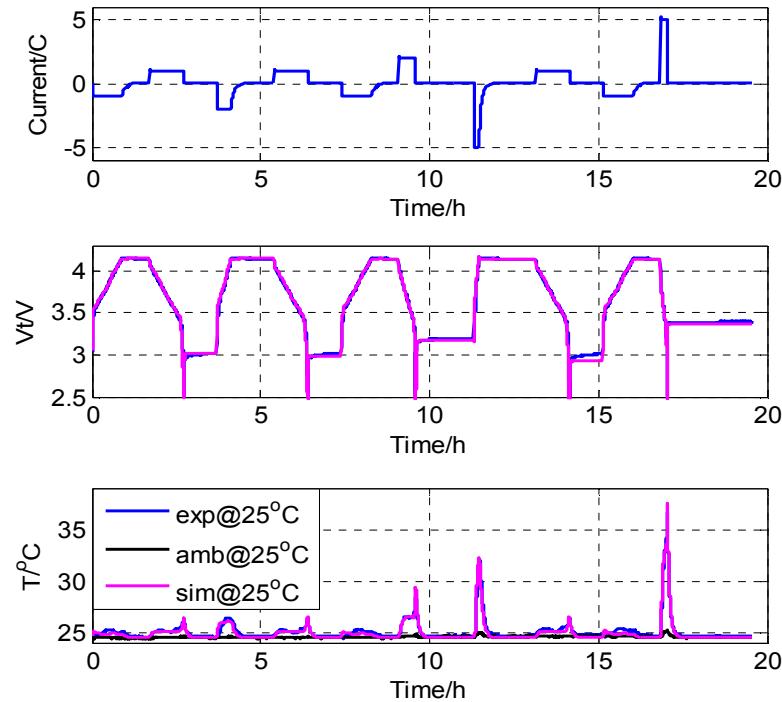
EDTA



European
Commission



Validation of the ROM at multiple cycles



Model	Full dischar.@1C	Full dischar.@2C	Full dischar.@5C
FOM	79	45	26
ROM	8.7	3.9	2.7

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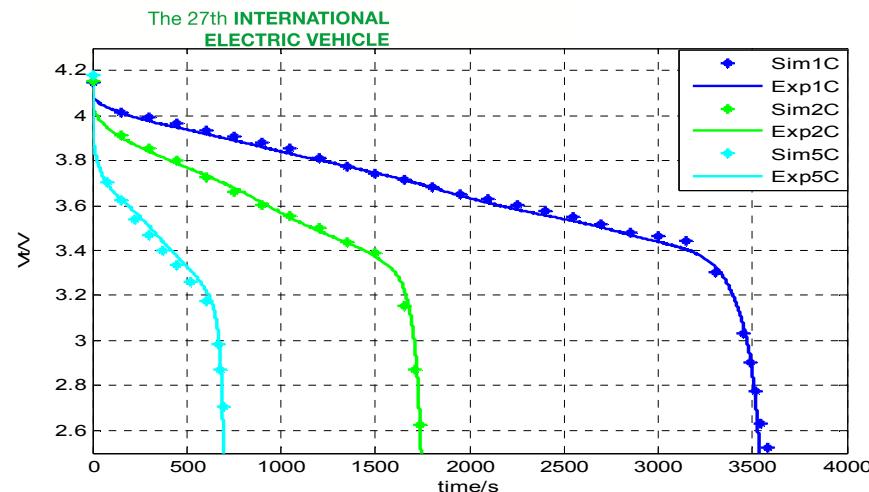


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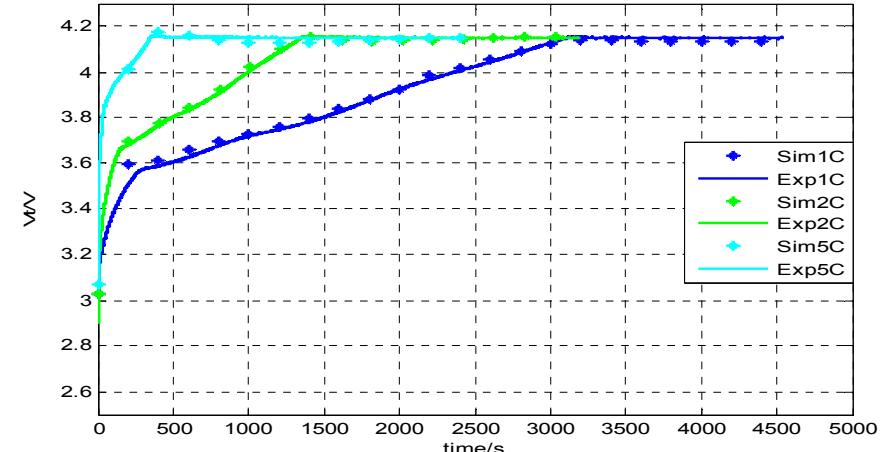


V_t @ 1/2/5C discharging at 25°C

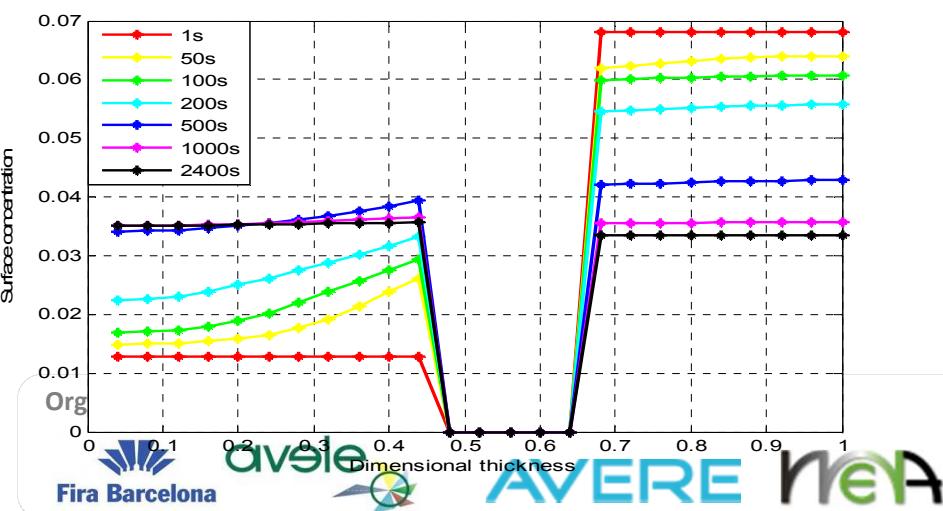
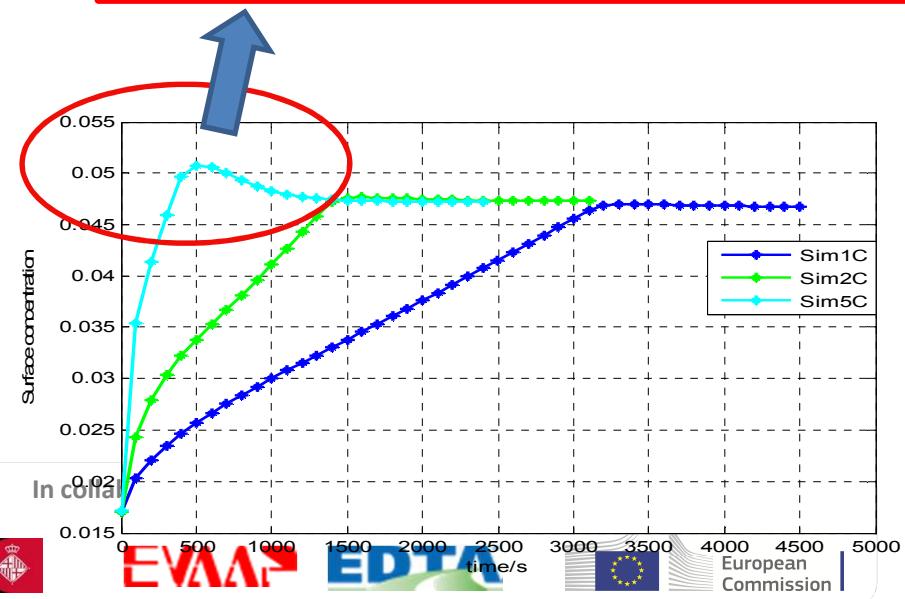
C_s @ 5C charging at 25°C

V_t @ 1/2/5C discharging at 25°C

C_s @ 1/2/5C charging at 25°C



High ion concentration



Model:	$\mathbf{x}_k = f(\mathbf{x}_{k-1}, \mathbf{u}_{k-1}, \mathbf{w}_{k-1})$ $\mathbf{z}_k = h(\mathbf{x}_k, \mathbf{v}_k)$	The domain equation for averaged concentration in solid particles is
Initialization:	Initial state estimation: $\hat{\mathbf{x}}_{k-1}$ Initial error covariance : \mathbf{P}_{k-1}	The domain equation for averaged concentration in negative electrode is
	Initial process noise covariance : \mathbf{W}_k	$\bar{c}_{s,\text{ave}}^k = \bar{c}_{s,\text{ave}}^{k-1} - 3 \frac{\Delta t}{R_s a_s F} \frac{I}{AL^-}$
	Initial measurement covariance : \mathbf{V}_k	The terminal voltage V_t is the difference between OCV and overpotential η ;
Time update:	State prediction: $\hat{\mathbf{x}}_k^- = f(\hat{\mathbf{x}}_{k-1}, \mathbf{u}_{k-1}, 0)$	$V_t = U_{\text{OCV}}^+(\bar{y}) - U_{\text{OCV}}^-(\bar{x}) - \eta$
	Error covariance prediction: $\mathbf{P}_k^- = \mathbf{A}_k \mathbf{P}_{k-1} \mathbf{A}_k^T + \mathbf{W}_k \mathbf{Q}_{k-1} \mathbf{W}_k^T$	$\bar{x} = \frac{\bar{c}_{s,\text{ave}}^-}{\bar{c}_{s,\text{max}}}, \bar{y} = \frac{\bar{c}_{s,\text{ave}}^+}{\bar{c}_{s,\text{max}}^+}$
Measurement update:	Kalman gain: $\mathbf{K}_k = \mathbf{P}_k^- \mathbf{H}_k^T (\mathbf{H}_k \mathbf{P}_k^- \mathbf{H}_k^T + \mathbf{V}_k \mathbf{P}_{k-1} \mathbf{V}_k^T)^{-1}$	The block diagram of the EKF based ROM:
	State correction: $\hat{\mathbf{x}}_k = \hat{\mathbf{x}}_k^- + \mathbf{K}_k (\mathbf{z}_k - h(\hat{\mathbf{x}}_k^-, 0))$	
	Error covariance correction: $\mathbf{P}_k = (\mathbf{I} - \mathbf{K}_k \mathbf{H}_k) \mathbf{P}_k^-$	

$$\frac{d}{dt} c_{s,\text{ave}} + 3 \frac{j^{\text{Li}}}{R_s a_s F} = 0$$

$$\bar{c}_{s,\text{ave}}^k = \bar{c}_{s,\text{ave}}^{k-1} - 3 \frac{\Delta t}{R_s a_s F} \frac{I}{AL^-}$$

$$V_t = U_{\text{OCV}}^+(\bar{y}) - U_{\text{OCV}}^-(\bar{x}) - \eta$$

$$\bar{x} = \frac{\bar{c}_{s,\text{ave}}^-}{\bar{c}_{s,\text{max}}}, \bar{y} = \frac{\bar{c}_{s,\text{ave}}^+}{\bar{c}_{s,\text{max}}^+}$$

Results of the EKF based ROM

Test condition:

Mode: JS

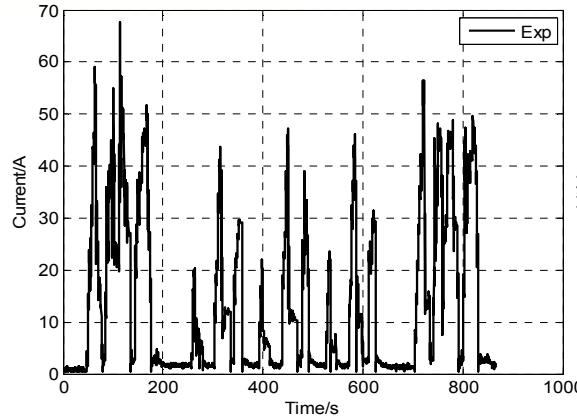
Temperature: 25°C

Initial SOC: 100%

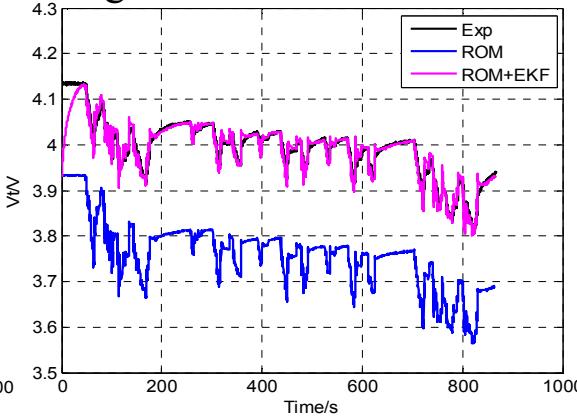
Initial error: 0.2V

(30% SOC)

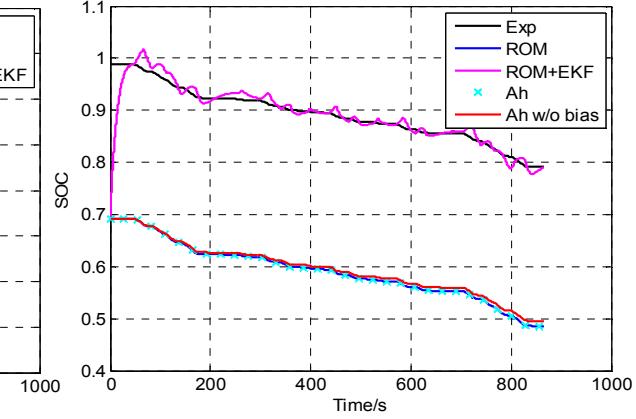
Current:



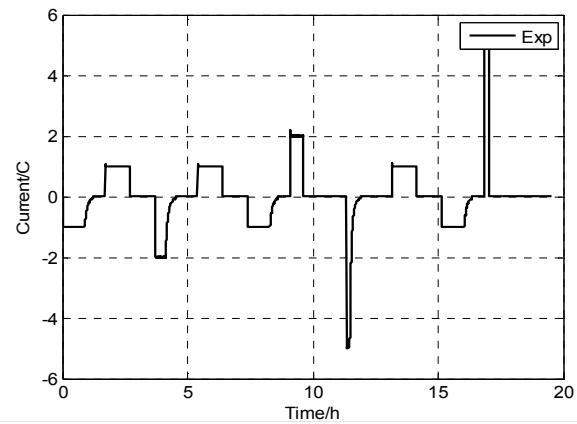
Voltage:



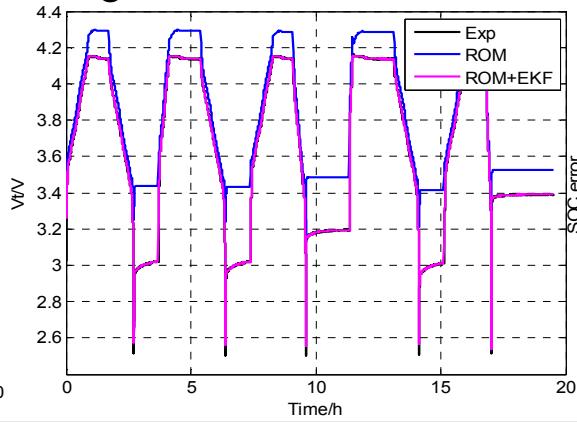
SOC:



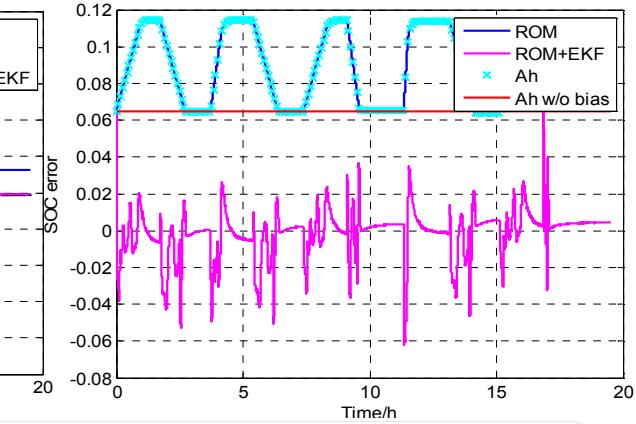
Current:



Voltage:



Error of SOC:



Test condition:

Mode: Depleting

Temperature: 25°C

Initial SOC: 0%

Initial error: 0.5V

(6.5% SOC)

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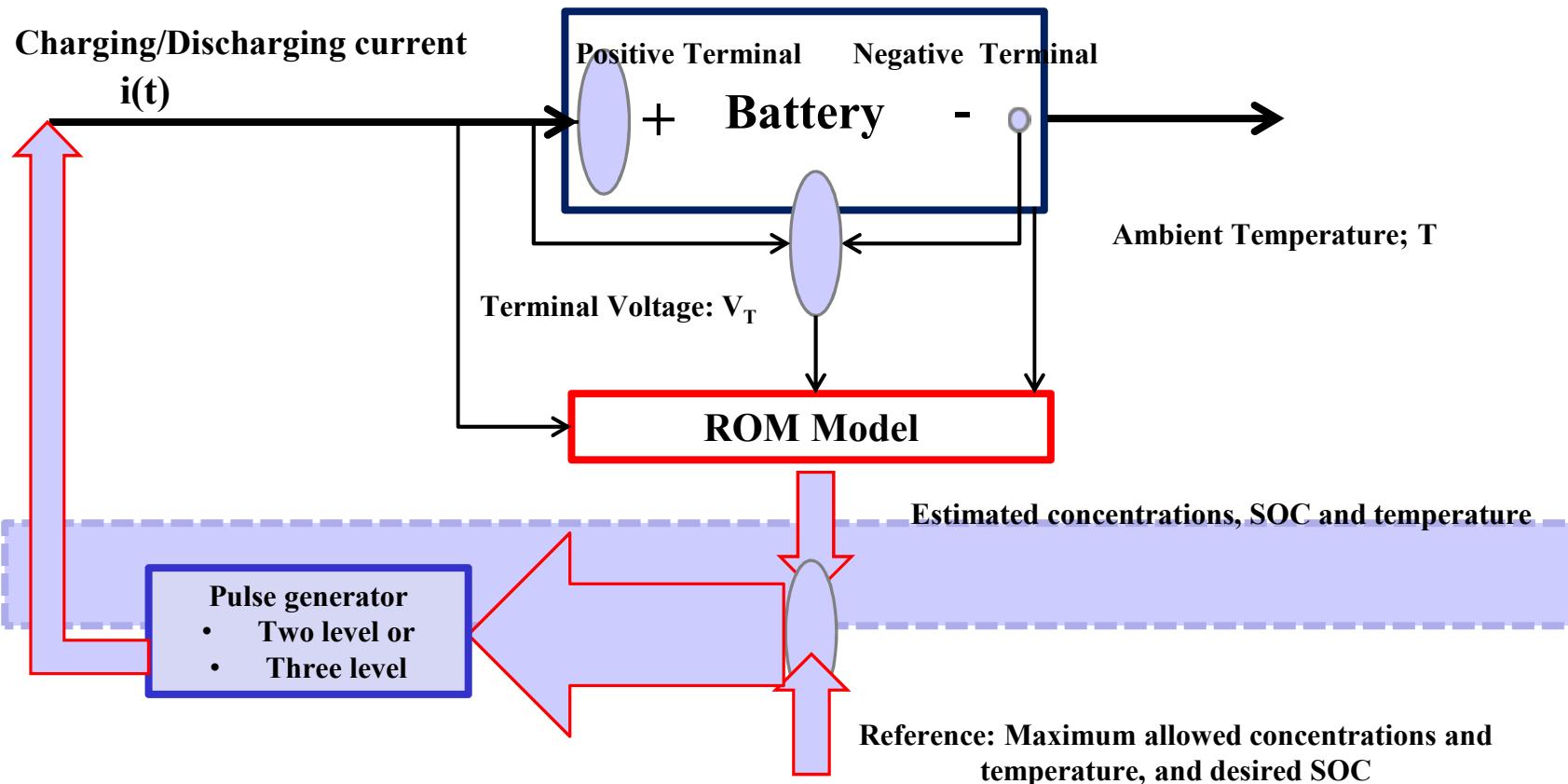
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New Charging method



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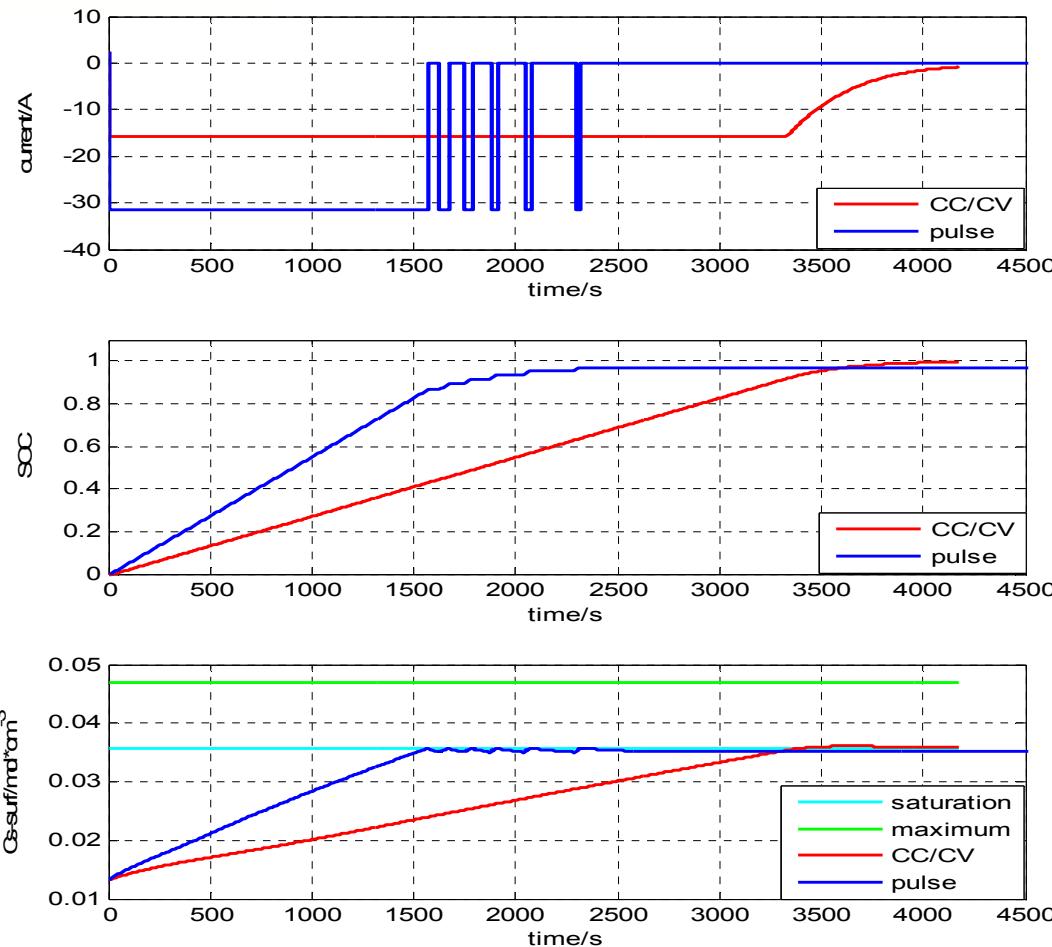
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Simulation Results of Fast Charging method



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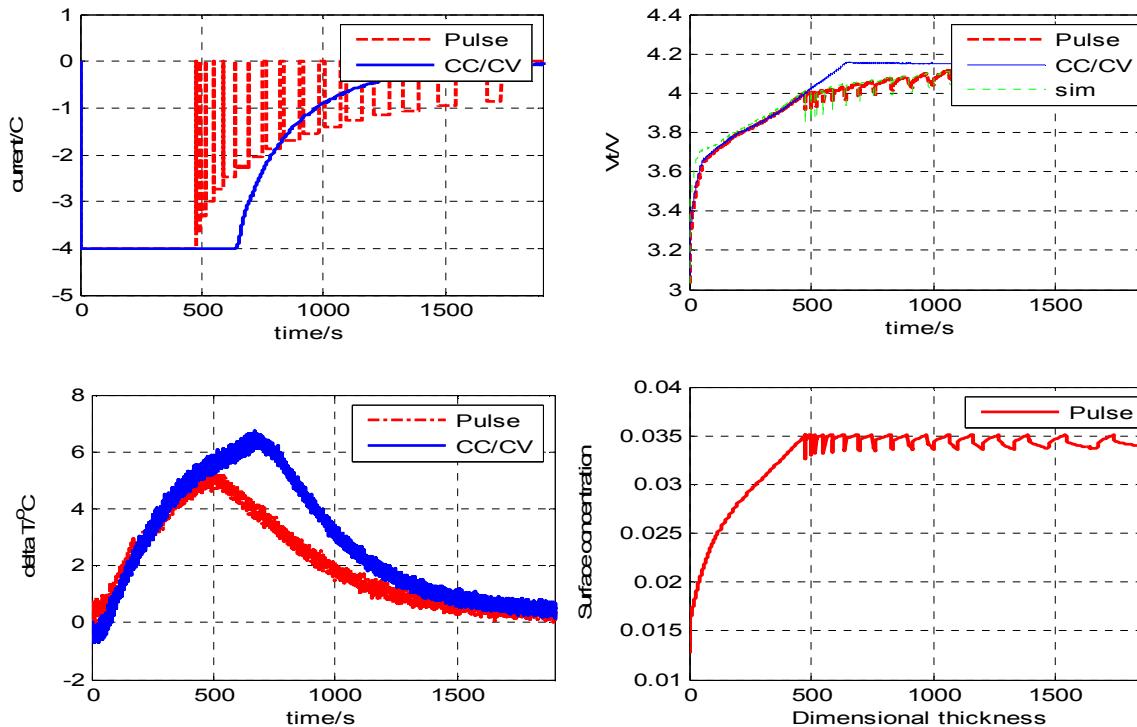
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Experimental results of the proposing Fast charging method



- Reduction of Charging time in an amount of 30-40%
- Less heat is generated
- Surface concentration can be kept under upper limitation that slows down Lithium-plating

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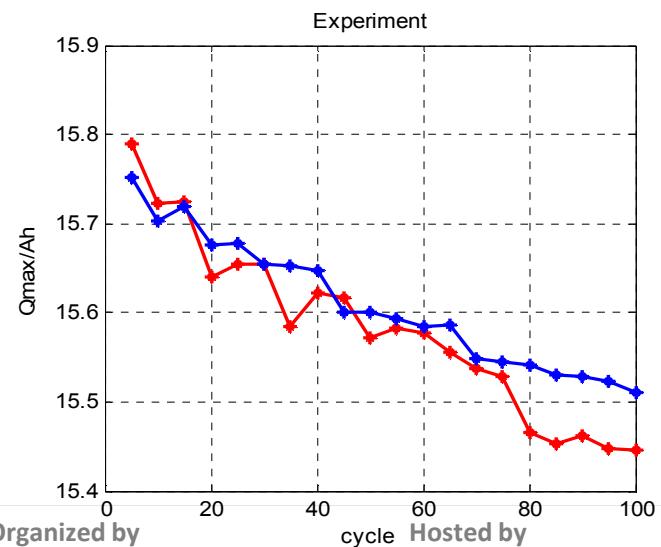


Fast Charging Algorithm

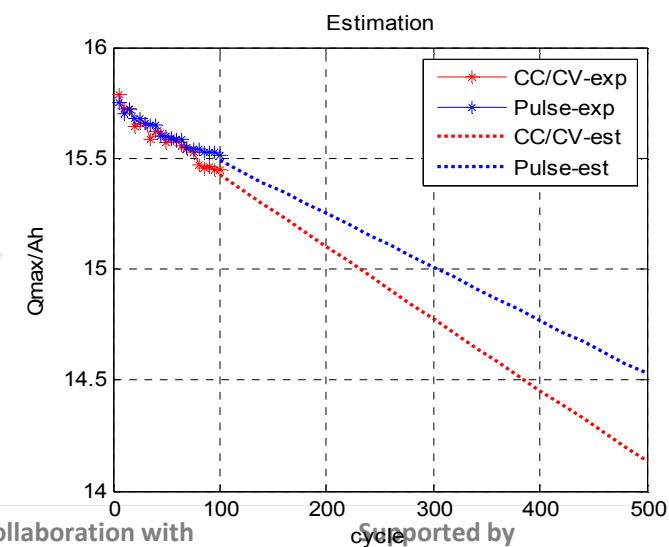
Test conditions:

Cell No.	1	2
Ambient temperature (°C)	25	25
Charging method	CC/CV	Pulse
Charging current (C)	4	4
Discharging current (C)	2	2
Rest time (min)	10	10
Cycles	100	100

- Less capacity fade: 0.24Ah after 100 cycles compared to 0.34Ah by the CC and CV.
- Proof of limitation of the surface concentration of particles in the negative electrode and reduction of charging capacity losses by a relatively high charging current.



If there is no significant
degradation



New fast charging algorithm is proposed

- **Development of a reduced Order Model based on electrochemical thermal model**
- **Design of SOC estimator based on EKF**
- **Validation of the model and SOC estimation at different current profiles**

Preliminary experimental results show;

- **Reduction of charging time up to 30-40%**
- **Reduction of capacity fade up to 6.3% at 100 cycles**
- **Less heat is generated**
- **SOC estimation errors less than 5 %**

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