Advances in electrochemical models for predicting the cycling performance of traction batteries: experimental study on Ni-MH and simulation

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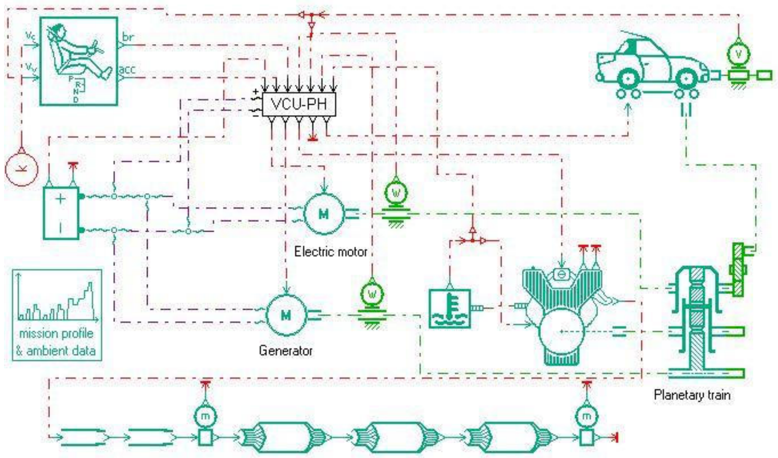
Purpose & goals

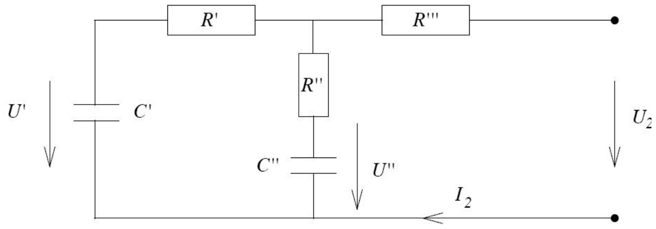
- Battery modeling
  - for precise on board State-of-Charge (SoC) estimation in Battery Management System (BMS)
  - for accurate battery simulation in HEV simulator to optimize the hybrid architecture design



➡ Develop and validate an advanced 0D model of a Ni-MH battery pack

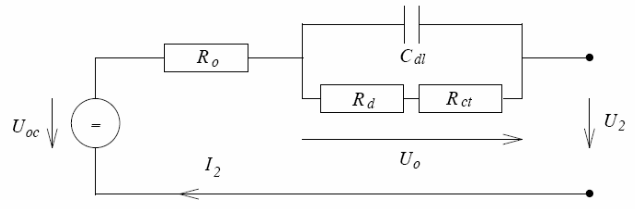
State of the art: battery models (1)

- Equivalent-circuit models
  - Black box: non-physical circuit topology that attempts at reproducing the main battery dynamics
  - Grey box: circuit elements try to reproduce the inner electrochemical behavior of the cells
  - Intuitive and easy to handle



But :

  - rely on the collection of look-up tables
  - circuit elements are parameterized as a function of SoC



➡ No accurate estimation of SoC while dealing with realistic operating conditions

State of the art: battery models (2)

- Electrochemical models
  - Based on the fundamental mechanisms and relates battery design with parameters linked to micro and macro information
  - SoC is calculated from the reactant concentrations, which are dynamic states updated with mass and charge balance equations

➡ *Soc is an internal parameter*

But :

- Sophisticated models are time consuming
- Simplifications readily available do account for transport phenomenon in the battery materials

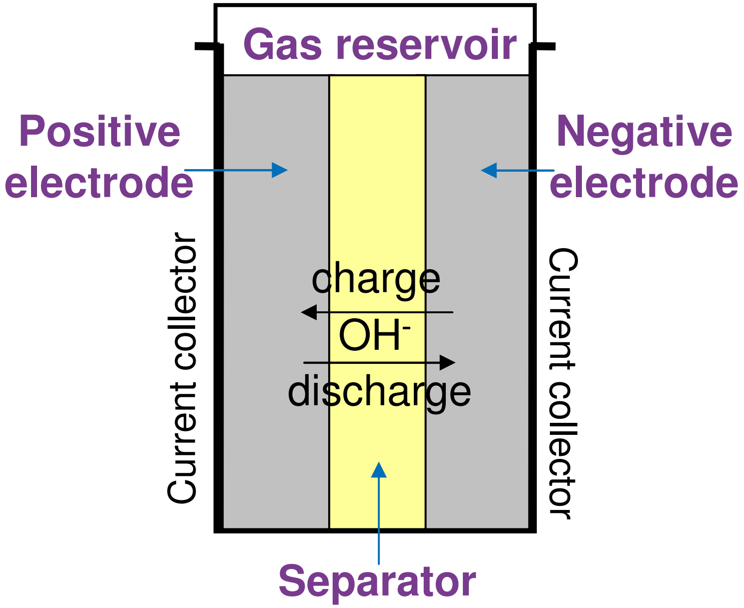
➡ Necessary to develop an advanced 0D-electrochemical model (lumped parameter model)

Outline

- Ni-MH battery modeling
- Experimental set-up
- EIS results
- Model calibration and evaluation
- Discussions & perspectives

Ni-MH battery

- Four regions
  - Ni oxide positive electrode - MH negative electrode - Porous separator - Gas reservoir
- Three phases
  - Solid Ni cylinders and MH spheres
  - Aqueous solution of KOH as the electrolyte
  - Gaseous oxygen



- Reactions

Positive electrode :

$NiOOH\ (s) + H_2O\ (l) + e^- \leftrightarrow Ni(OH)_2\ (s) + OH^-\ (aq)$ (1)

$\frac{1}{2} O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$ (2)

Negative electrode :

$M\ (s) + H_2O\ (l) + e^- \leftrightarrow MH\ (s) + OH^-\ (aq)$ (3)

$\frac{1}{2} O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$ (4)

Model assumptions (1)

- Classical 0D approach: all quantities are homogeneous in each cell region
- Advanced 0D electrochemical model proposed to account for transport phenomena
  - Use of a localized concentration discontinuity:
    - mean concentration in the bulk of active material particles differs from the concentration at the interface
    - oxygen concentration in the bulk of electrolyte / at the interface differ
  - Double layer capacitances are introduced for each electrode to take into account spatial ionic charge accumulation at the electrode / electrolyte interfaces

Model assumptions (2)

- Liquid/gas interfacial equilibrium for the oxygen links the dissolved oxygen concentration to the gaseous oxygen pressure via the Henry law
- Potential hysteresis is considered
- Thermal effects are adequately taken into account by introducing an energy balance equation for the whole cell.

Model equations

- The kinetics of reactions (1)–(4) are derived from the general Butler-Volmer equations:

$$J(t) = J_0 \left\{ \frac{\prod_{j=1}^{N'} [P_j]_t^{o_{pj}}}{\prod_{j=1}^{N'} [P_j]_{eq}^{o_{pj}}} \exp\left(\frac{\alpha_{ox} nF\eta(t)}{RT} \right) - \frac{\prod_{i=1}^{N} [R_i]_t^{o_{rj}}}{\prod_{i=1}^{N} [R_i]_{eq}^{o_{rj}}} \exp\left(-\frac{\alpha_{red} nF\eta(t)}{RT} \right) \right\} \exp\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right)$$

- Equilibrium potentials depends on interfacial concentration in nickel and temperature

$$\eta_1 = \Delta\Phi_{pos} - \left(\left(1 - 2\frac{\bar{c}_{Ni}}{c_{Ni,max}} \right) K_{inter} \frac{RT}{F} + (T - T_0)\frac{dU_1}{dT} + U_{eq,ref,1} \right)$$

$$\eta_2 = \Delta\Phi_{pos} - \left(U_{0std,2} + (T - T_0)\frac{dU_2}{dT} \right)$$

$$\eta_3 = \Delta\Phi_{neg} - \left(U_{0std,3} - \frac{RT}{F}\mu \ln(c_{MH,ref}) + (T - T_0)\frac{dU_3}{dT} \right)$$

$$\eta_4 = \Delta\Phi_{neg} - \left(U_{0std,4} + (T - T_0)\frac{dU_4}{dT} \right)$$

Model equations

- Conservation equations
  - Mass balance

$$\frac{dc_{Ni}}{dt} = -\frac{J_1}{l_{y,pos}F}$$

$$\frac{dc_{MH}}{dt} = -\frac{J_3}{l_{y,neg}F}$$

$$\frac{dp_{O2}}{dt} = \frac{10RT}{V_{gas}} \cdot \frac{S_{pos}J_2 + S_{neg}J_4}{4F}$$

  - Charge balance

$$\frac{d\Delta\Phi_{pos}}{dt} = \frac{1}{C_{dl,pos}}\left(\frac{I_{cell}}{S_{pos}} - J_1 - J_2\right)$$

$$\frac{d\Delta\Phi_{neg}}{dt} = \frac{1}{C_{dl,neg}}\left(-\frac{I_{cell}}{S_{neg}} - J_3 - J_4\right)$$

$$V_{cell} = \Delta\Phi_{pos} - \Delta\Phi_{neg} + R_{int}I_{cell}$$

  - Energy balance (thermal effects)

$$\frac{dT}{dt} = \frac{1}{M_{cell}C_p}(\varphi_{gen} - \varphi_{tra})$$

$$\varphi_{gen} = V_{cell}I_{cell} - \sum_{z=1}^{4} J_z\left(U_{0std,z} - T_0\frac{dU_z}{dT}\right)S_{(z)}$$

$$\varphi_{tra} = h_{cell}A_{cell}(T - T_a)$$

- State-of-Charge: $q = 1 - \dfrac{c_{Ni}}{c_{Ni,max}}$

Model summary

- 15 internal variables:
  - J_1, ... J_4, η_1, ... η_4, $\Delta\Phi_{pos}$, $\Delta\Phi_{neg}$, c_{Ni}, c_{MH}, P_{O2}, T, v_{cell}
- 15 equations
- About 50 parameters
  - parameters selected according to the literature (J_{0i}, U_{oi}, H...)
  - parameters directly measured:
    - geometric parameters (surfaces, thicknesses, porosity...)
    - electrode nature, electrolyte composition
    - electrochemical parameters (double layer capacitance, internal resistance...)
  - parameters adjusted according to measurements

→ Experimental study on commercial 6,5 Ah Ni-MH cells and pack

Experimental

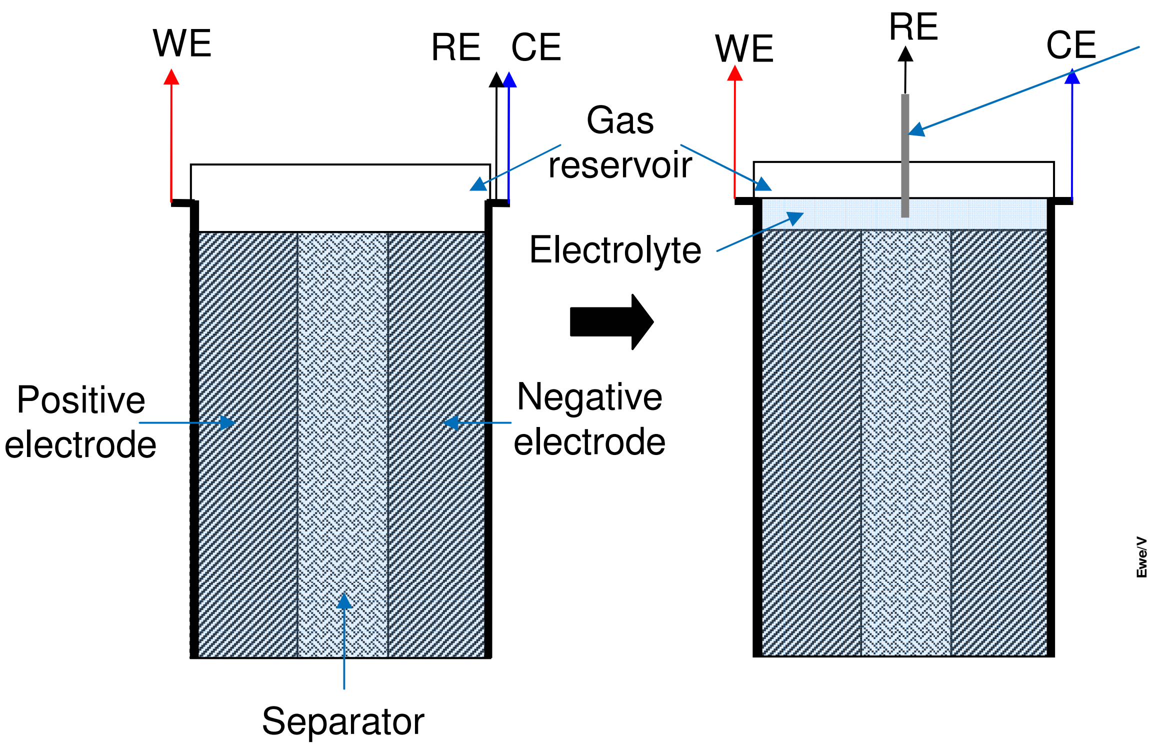
- Commercial sealed Ni-MH battery pack (202 V, 168 serially connected cells)

- Post-mortem analysis on cell components

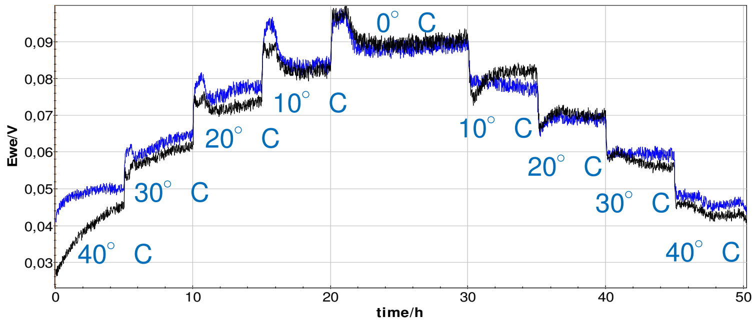
  (SEM, X-ray diffraction, porosimetry, pH dosage)
- Electrical measurements on single cell with or without introduction of a reference electrode using a potentiostat
  - charge/discharge, capacity measurements
  - Electrochemical Impedance Spectroscopy (EIS)
- Electrical measurements on the entire battery pack using a 500A/500V Digatron test bench
  - Hybrid Pulse Power Characterization (HPPC)

3-electrode experimental set-up

- Commercial Ni-MH cell before and after insertion of the reference electrode.



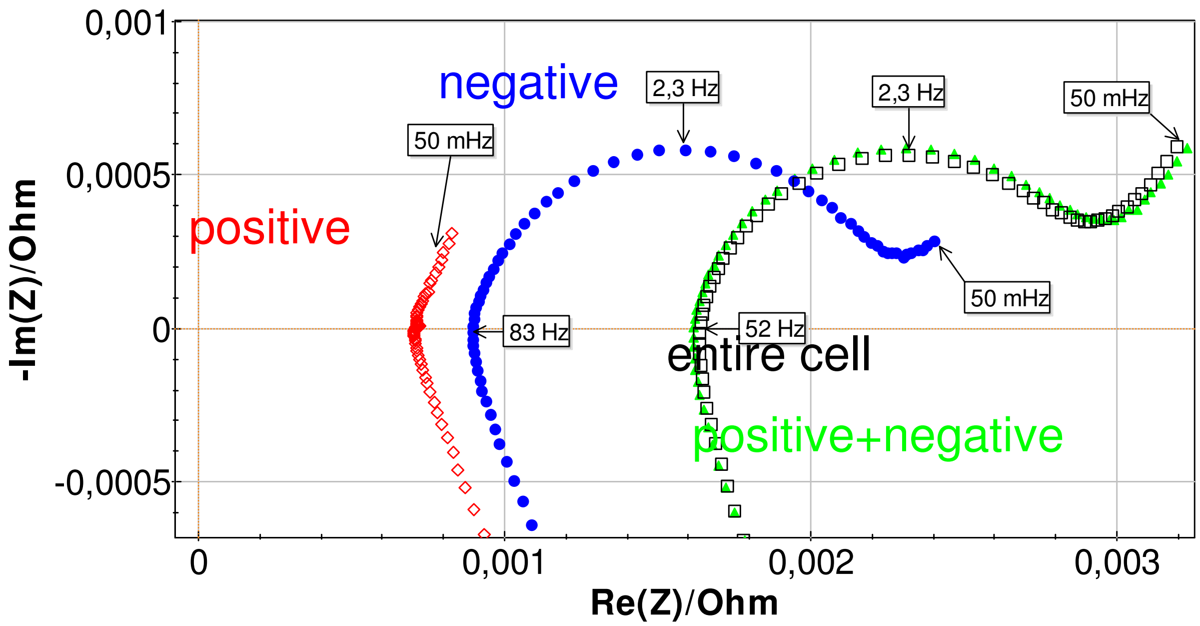
Study of the potential of a Pt wire immersed in the KOH electrolyte at constant temperature and constant OH^- concentration



➡ Constant and reproducible potential of the Pt wire assessed as reference electrode

EIS measurements (1)

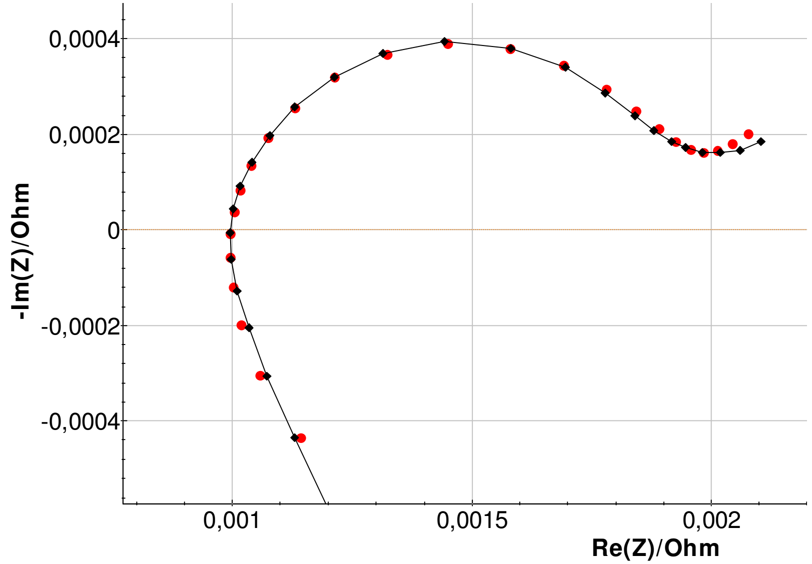
- EIS diagrams of a Ni-MH commercial cell modified with a reference electrode at SoC=50%, 20°C.

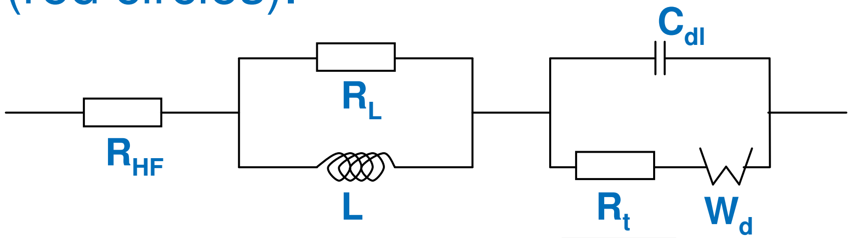


Validity of the 3 electrodes measurements
Note the major contribution of the negative electrode

Parameters extraction (1)

- Nyquist diagram of the negative electrode at SoC=50%, 20°C and the equivalent circuit model (red circles).





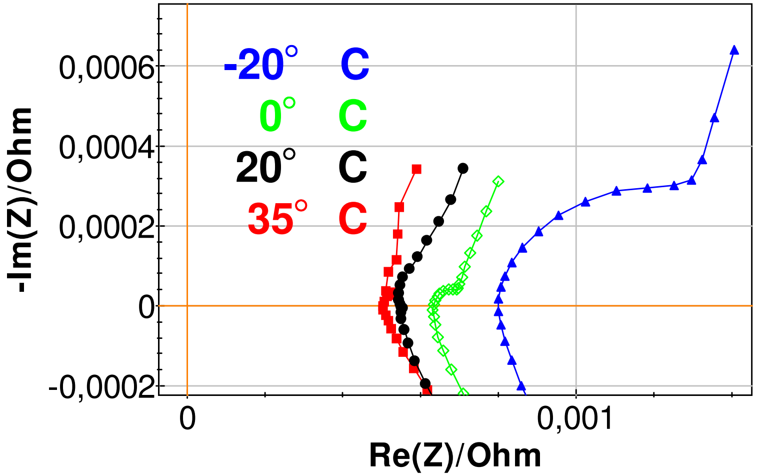
Warburg : $Z(f) = R_d \dfrac{th(\sqrt{t_d\, j2\pi f}\,)}{\sqrt{t_d\, j2\pi f}}$

R_{HF}	$0,977.10^{-3}\,\Omega$
C_{dl}	45,73 F
R_t	$0,946.10^{-3}\,\Omega$
R_d	$1,234.10^{-3}\,\Omega$
t_d	81,14 s
L	$0,127.10^{-6}$ H
R_L	$1,391.10^{-3}\,\Omega$

➡ Estimation of the double layer capacitance Cdl_{neg} directly injected in the model

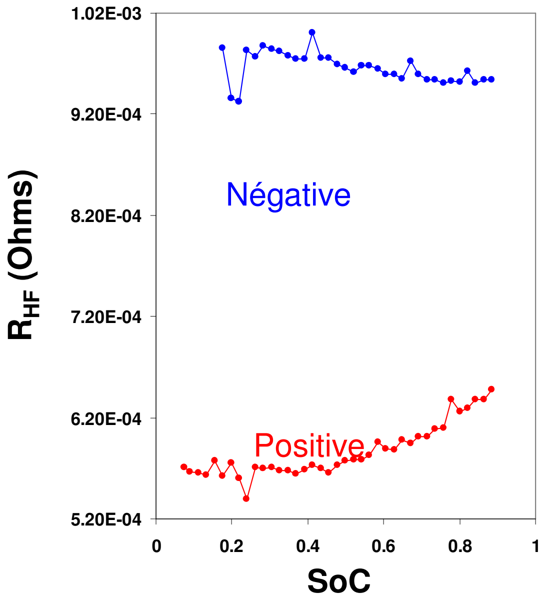
Parameters extraction (2)

Negative electrode at SoC=50%



→ Cdl of the positive measured at low temperature

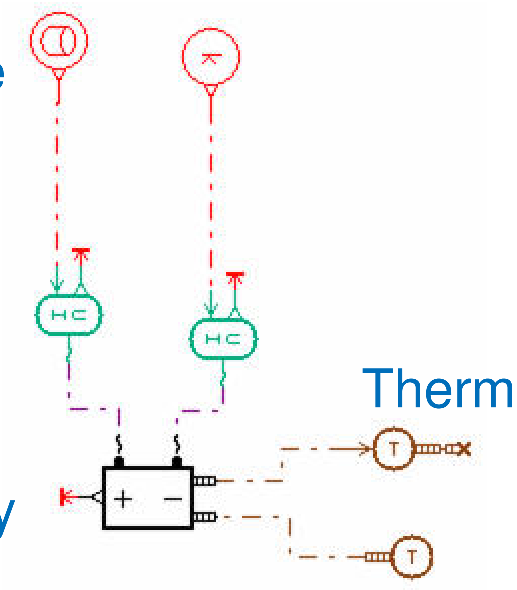
Evolution of the R_{HF} of the positive and the negative electrode with the SoC (20°C)



→ Internal resistance taken as constant

Model calibration and simulation (1)

- Simulation sketches in AMESim environment for battery cycling

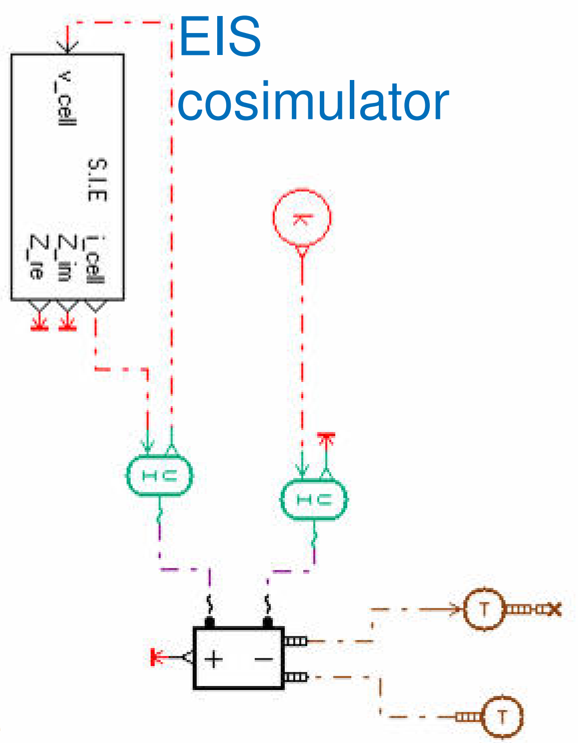


Source

Thermal port

Battery

- Simulation sketches in AMESim environment for EIS simulation

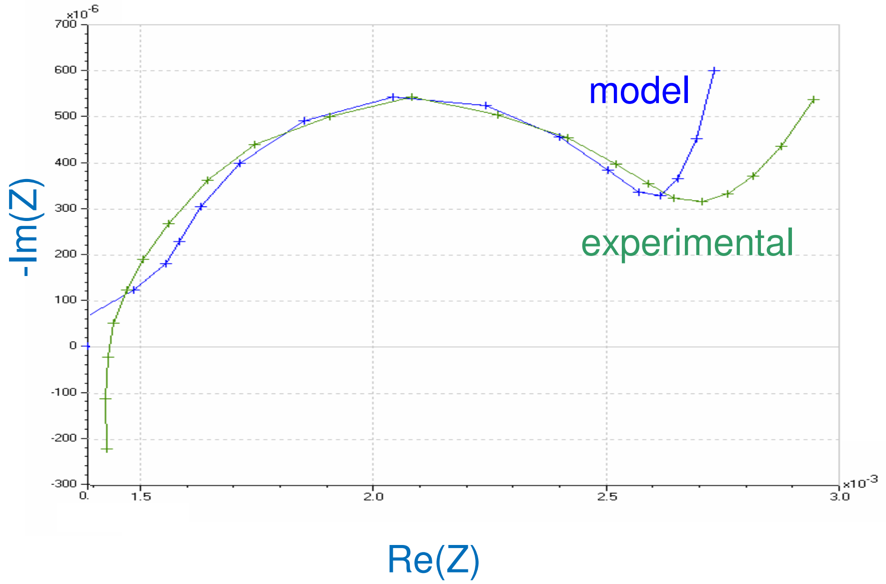


EIS cosimulator

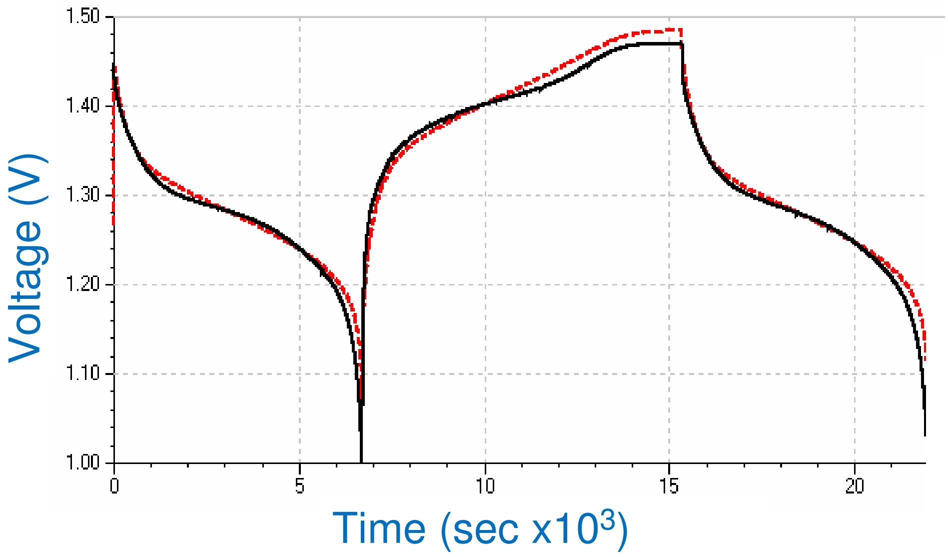
➡ EIS simulator able to reproduce experimental test cases

Model calibration and simulation (2)

- Comparison of the experimental and simulated EIS diagram (SoC 60%):



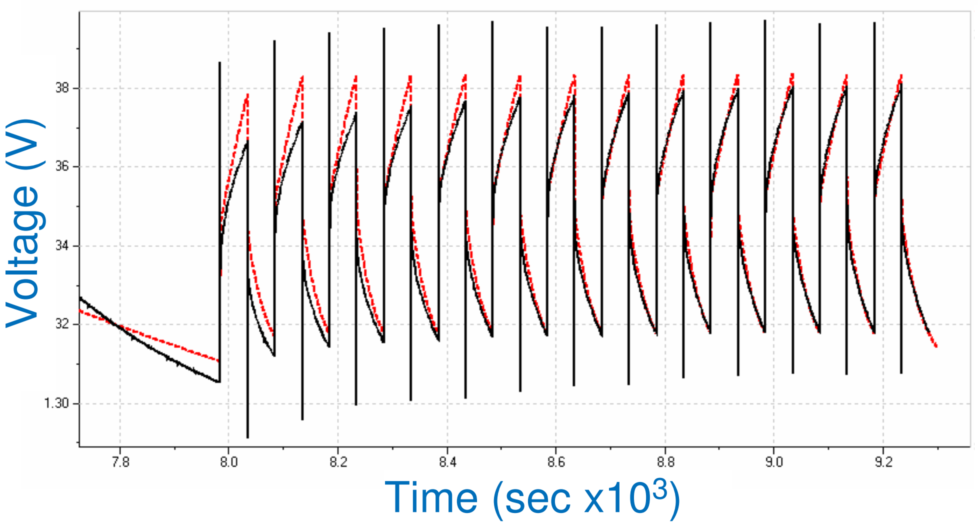
- Comparison of the experimental and simulated voltage evolution during C/2 rate charge/discharge cycles:



➡ Tuning of 5 remaining model parameters with two experimental cases

Model evaluation on a cell

- Comparison of the cell voltage of a Ni-MH cell during C rate cycling (alternation +C / -C during 50s) with the simulation.

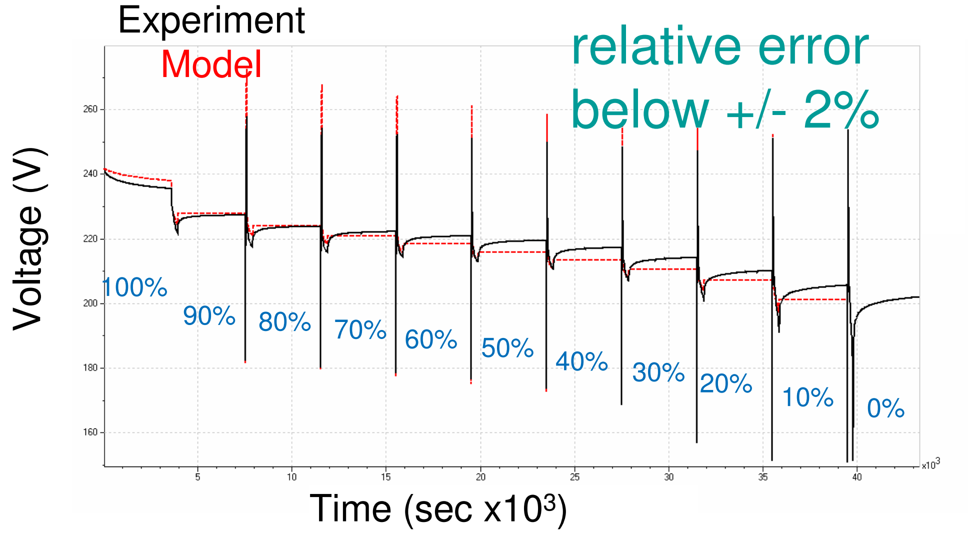


error +/- 0,8%

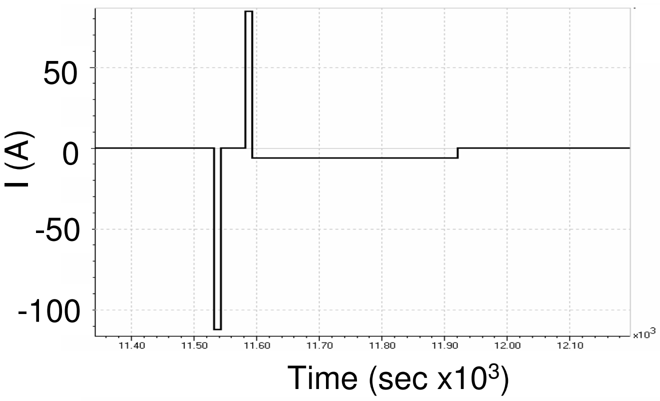
Model validation on a slow C-rate dynamic profile at 20° C

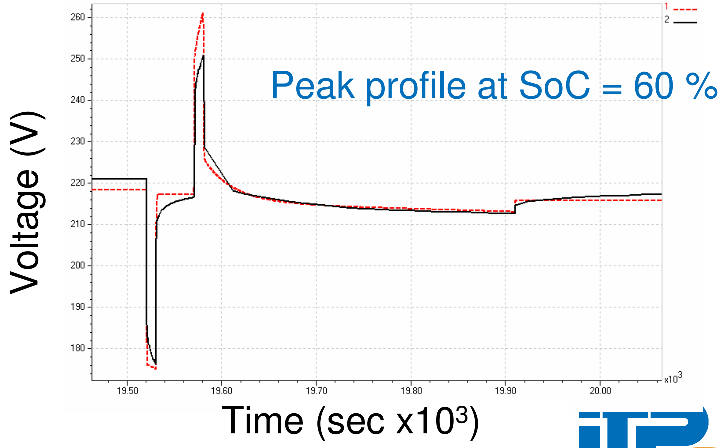
Model evaluation on a pack

- Comparison of measured and simulated Ni-MH battery pack voltage during a high current Hybrid Pulse Power Characterisation Test (HPPC, FreedomCar Manual):



relative error below +/- 2%



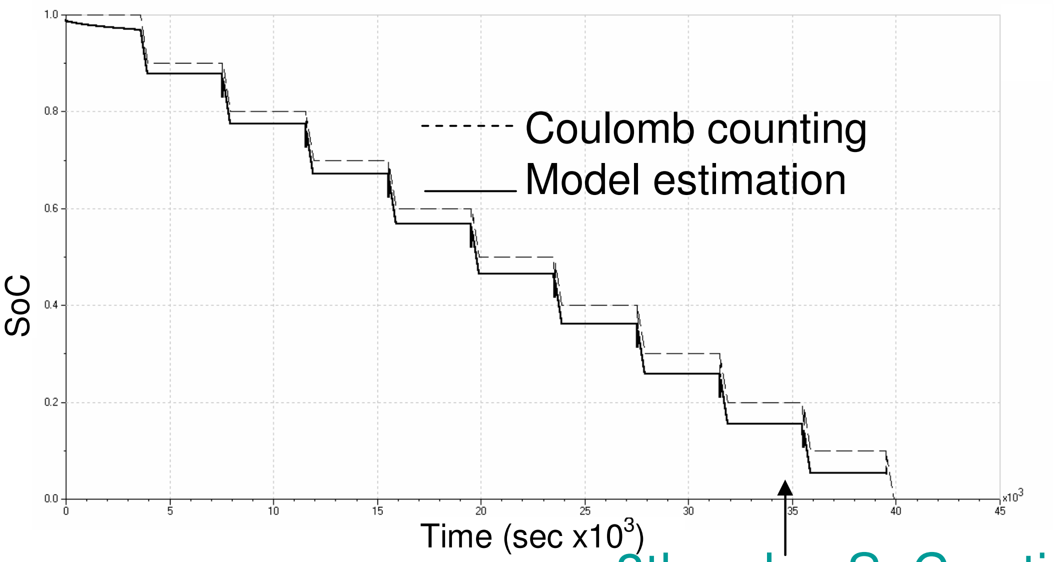


Peak profile at SoC = 60 %

➡ Model validation in highly dynamic conditions under high currents at 20° C

Discussion

- Comparison of simulated SoC evolution with SoC evolution obtained from the coulomb counting method during a high current HPPC test:



8th pulse SoC estimated at 5% by the model and 10% by CC

➡ Model prediction explains the experimental limitation observed in the 9th pulse, not coulomb counting

Perspectives

- Advanced 0D electrochemical model very promising for reliable real time SoC monitoring

  ➡ *Basis to design a Kalman filter to be used in BMS for control applications*

- Further work in progress
  - to better account for relaxation periods
  - to validate thermal and pressure predictions
  - to take into account battery aging

- Other model developments
  - on Li-ion batteries

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