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Lithium-ion batteries modelling: a simple fractional differentiation based model and its associated parameters estimation method

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Abstract – This paper deals with lithium-ion batteries modelling. From an electrochemical model available in the literature, several assumptions and simplifying hypothesis are proposed in order to get a simpler but accurate model. The obtained model is based on a fractional transfer function resulting in the resolution of a partial differential equation that describes the lithium ion diffusion inside the electrodes. The model involves only three parameters and a polynomial that fits the open circuit voltage of the battery. A method to estimate the model parameters and the polynomial is proposed. A single discharge test (constituted of several discharge steps) is required to operate the parameter estimation method. The accuracy for battery voltage prediction of the resulting model is evaluated with various tests.

Keywords – Lithium-ion batteries, fractional models, parameters estimation.

I. INTRODUCTION

To ensure safe and reliable hybrid or electric vehicles operation involving lithium-ion batteries, car manufacturers have associated a Battery Management System (BMS) to the battery pack. This system has estimating functions (State of Charge (SOC), State of Health (SOH), and temperature), prediction functions (voltage, power, and energy), thermal management function (Chatzakis, 2003). For such functions, a BMS often uses battery models. Accuracy of the estimated and predicted information by the BMS thus depends on the model accuracy. However, accuracy must not be at the cost of a complex model. The resulting model must be easily implemented in a car microcontroller and must not be large resources consuming.

This paper proposes a new dynamical model for a lithium-ion battery in order to give an answer to the dual objective mentioned above. An extensive analysis on lithium ion batteries modeling is proposed in (Sikha et al, 2005) and permits to conclude that many models exist in the literature for this kind of batteries. The two main classes are empirical electric models (Buller, 2005) and reduced rigorous electrochemical models. Fuzzy models are a significant part of the proposed models (Sinh et al, 2006). The originality of this paper lies in how the proposed model is obtained and how its parameters are determined. It results in simplifications of an electrochemical model that describes the battery behavior using partial differential equations. Some of these simplifications were described in (Sabatier et al, 2013) and have allowed a first simplified model only based on

differential equations, but in which electrochemical variables and parameters still appear (parameters physical meaning is often lost with an approach based on model reduction). It is thus easier to implement in a car controller than the electrochemical model, and it keeps information about the physical system. This first simplified model is reminded in this paper because it is the starting point of our new work and also to highlights that it involves fractional differentiation. As shown on several electrochemical devices (Sabatier et al, 2006), (Bertrand et al, 2010), (Sabatier et al, 2010), (Cugnet et al, 2010), fractional differentiation permits to obtain models with a low number of parameters but that well capture the diffusion phenomena that take place inside a battery. The goal of the paper is to propose additional assumption to obtain a simpler model, less controller resources consuming. Such a model is thus easier to implement and remains accurate. It can thus be used for SOC or SOH estimator design.

II. ELECTROCHEMICAL MODEL

The simplified model that will be presented in the sequel is based on lithium-ion electrochemical model presented in (Smith et al, 2010) which result in Newman's modeling approach (Newman and Thomas-Alyea, 2004). This model is pseudo 2D and based on a representation of the cell such as in figure 1.

In figure 1, electrodes are seen as an aggregation of spherical particles (2D representation) in which the Li^+ ions are inserted. The first spatial dimension of this model, represented by variable x, is the horizontal axis. The second spatial dimension is the particle radius r.

Figure 1 - Pseudo 2D model of a lithium-ion cell

(Smith et al, 2010)

The cell is constituted of three regions (two electrodes and a separator) that imply four distinct boundaries at:

- $x = 0$: negative electrode current collector;

- $x \in \left]0; \delta_n\right[$: region 1, δ_n thickness negative carbon electrode (Li_xC_6, MCMB…);

- $x = \delta_n$: negative electrode / separator interface;

- $x \in \left]\delta_n; \delta_n + \delta_{sep}\right[$: region 2, δ_{sep} thickness separator;

- $x = \delta_n + \delta_{sep}$: separator / positive electrode interface;

- $x \in \left]\delta_n + \delta_{sep}; L\right[$: region 3, δ_p thickness positive electrode made of $LiCoO_2$ (or others);

- $x = L$: positive electrode current collector.

The two electrodes are assumed electrochemically porous. Regions 1 and 3 are therefore constituted of a solid phase (electrode material) and a liquid phase (electrolyte).

The cell is supposed supplied by a current $I(t)$. The cell voltage denoted $U(t)$ is defined by the relation:

$$U(t) = \phi_s(L,t) - \phi_s(0,t) - \frac{R_f}{A} I(t) \tag{1}$$

where $\phi_s(L,t)$ and $\phi_s(0,t)$ are respectively the positive electrode potential at abscissa $x = L$ and the negative electrode potential at abscissa $x = 0$; R_f denotes the contact résistance and A the electrodes surface. Note that all the parameters used in the following equation are defined in (Smith, 2006) and (Smith et al, 2010).

As described in (Smith, 2006) and (Smith et al, 2010), lithium concentration $c_s(x, r, t)$ evolution in the spherical particles of radius $r=R_s$, is supposed described by the diffusion law,

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial c_s}{\partial r} \right) \qquad \begin{cases} \left. \dfrac{\partial c_s}{\partial r} \right|_{r=0} = 0 \\[2mm] D_s \left. \dfrac{\partial c_s}{\partial r} \right|_{r=R_s} = \dfrac{-j^{Li}}{a_s F} \end{cases} \tag{2}$$

In relation (2), a_s and F denote respectively the active surface area per electrode unit volume (cm^2/cm^3), and Faraday's constant (96.487 C/mol).

Lithium concentration $c_e(x, t)$ in the electrolyte is modeled by:

$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial x}\left(D_e^{eff} \frac{\partial}{\partial x} c_e \right) + \frac{1 - t_+^o}{F} j^{Li}, \tag{3}$$

with

$$\left. \frac{\partial c_e}{\partial x} \right|_{x=0} = \left. \frac{\partial c_e}{\partial x} \right|_{x=L} = 0 . \tag{4}$$

In relation (3), ε_e, D_e^{eff} and t_+^o are respectively lithium volume fraction in the electrolyte, the effective diffusion coefficient and the transference number of lithium ions with respect to the velocity of solvent.

Charge conservation in the solid phase of each equation is defined by the Ohm's law:

$$\frac{\partial}{\partial x}\left(\sigma^{eff} \frac{\partial}{\partial x} \phi_s \right) - j^{Li} = 0, \tag{5}$$

with the following limit conditions at the current collectors:

$$-\sigma_-^{eff} \frac{\partial \phi_s}{\partial x}\bigg|_{x=0} = \sigma_+^{eff} \frac{\partial \phi_s}{\partial x}\bigg|_{x=L} = \frac{I}{A}, \tag{6}$$

and the null current conditions at the separator:

$$\frac{\partial \phi_s}{\partial x}\bigg|_{x=\delta_n} = \frac{\partial \phi_s}{\partial x}\bigg|_{x=\delta_n+\delta_{sep}} = 0 . \tag{7}$$

In relation (5), $\sigma^{eff}(x)$ is the effective conductivity of the solid matrix with $\sigma_-^{eff} = \sigma^{eff}(0)$ and $\sigma_+^{eff} = \sigma^{eff}(L)$.

If $\phi_e(x, t)$ denotes the electrolyte potential, charge conservation in the electrolyte is defined by:

$$\frac{\partial}{\partial x}\left(\kappa^{eff} \frac{\partial}{\partial x}\phi_e\right) + \frac{\partial}{\partial x}\left(\kappa_D^{eff} \frac{\partial}{\partial x}\ln(c_e)\right) + j^{Li} = 0 , \tag{8}$$

with:

$$\frac{\partial \phi_e}{\partial x}\bigg|_{x=0} = \frac{\partial \phi_e}{\partial x}\bigg|_{x=L} = 0 . \tag{9}$$

In relation (8), κ^{eff} and κ_D^{eff} are respectively the effective ionic conductivity and the effective diffusional conductivity.

The four differential equations (2), (3), (5) and (8) that describe variables $c_{s,e}, c_e, \phi_s, \phi_e$ variations are linked by the Butler-Volmer equation (Bockris et al, 2000).

$$j^{Li} = a_s i_o \left\{ \exp\left[\frac{\alpha_a F}{RT}\eta\right] - \exp\left[-\frac{\alpha_c F}{RT}\eta\right] \right\}. \tag{10}$$

In (10), i_0 denotes the exchange current density, T is the temperature (K) and R is the universal gas constant (8.3143 J/mol K). j^{Li} is induced by overvoltage η, defined by the potential difference between the solid phase and the electrolyte, and equilibrium thermodynamic potential U_i:

$$\eta_i = \phi_{s\,i} - \phi_{e\,i} - U_i . \tag{11}$$

The subscript $i \in \{n, p\}$ is used to denote the negative electrode as $i=n$ and the positive electrode as $i=p$ ($i=s$ can also be used for the separator). The equilibrium potential U_i is a function of the ratio of lithium concentration at the spherical particle surface (in the solid phase) by the maximal value of this concentration. For the two electrodes, the equilibrium potentials are thus defined by:

$$U_n = f_n(X) \quad \text{and} \quad U_p = f_p(Y), \tag{12}$$

where

$$X = \frac{C_{sn\_e}}{C_{s\max\_n}} \quad \text{and} \quad Y = \frac{C_{sp\_e}}{C_{s\max\_p}} . \tag{13}$$

System input is the current $I(t)$ in equation (6). System output is the cell voltage given by relation (1).

III. FROM THE ELECTROCHEMICAL MODEL TO A FRACTIONAL DYNAMICAL MODEL

The electrochemical model previously described has been implemented under Comsol Multiphysics and its parameters have been adjusted to fit a SAFT VL7P battery (VL7P reference of the SAFT society) behavior. This model was then used to speculate for assumptions and simplifications presented in (Sabatier et al, 2014). These assumptions have allowed the first simplified model presented in figure 2, in which electrochemical variables and parameters still appear (parameters physical meaning is often lost with an approach based on model reduction) but only based on differential equations. This model is thus easier to implement in a car controller than the electrochemical model. In figure 2 model, the transfer functions $H_{cei}(s)$, $i \in \{n, p\}$, link the current $I(s)$ to the electrolyte concentration at the abscissa δ_n and δ_p and are defined by:

$$H_{cei}(s) = \frac{C_e(\delta_i, s)}{I(s)} = \frac{K_{cei}}{1 + \dfrac{s}{\omega_{cei}}} . \tag{14}$$

Transfer functions $H_{csi,e}(p)$, $i \in \{n, p\}$, link the mean value of the lithium current density in electrode, denoted $J^{Li}_{i\_mean}(s)$, to the lithium concentration at the surface of the spherical particles. There are fractional transfer functions defined by:

$$H_{csi,e}(s) = \frac{c_{si,e}(s)}{J^{Li}_{i\_mean}(s)} = \frac{K_{1i}\left(1 + \dfrac{s}{\omega_{csei}}\right)^{0.5}}{s} . \tag{15}$$

Variables C_{si_0}, $i \in \{n, p\}$, in figure 1 denote the initial lithium concentration in the spherical particles. The linearized Butler-Volmer equation is defined by:

$$j^{Li}_{i\_mean} = \frac{a_{si} i_{0i} F}{RT}(\alpha_a + \alpha_c)\eta_i . \tag{16}$$

The goal now is to propose additional assumptions (in relation to those proposed in (Sabatier et al, 2004)) to obtain a simpler model, less microcontroller resources consuming.

Figure 2 : *First simplified model obtained*

Assumption H₅

To obtained model in figure 2, lithium concentration in the separator has been supposed a linear function of x around the initial value denoted $C_{ei}(x,0)$, $i \in \{n, p\}$. As shown in figure 3, this concentration varies slightly around an average value. It is thus now assumed that the lithium concentration in the electrolyte and in the separator is constant, that is:

$$c_e(x,t) = Cst \qquad \forall x \in [\delta_n, \delta_p].$$ (17)

According to this assumption, the difference $c_e(\delta_p, t) - c_e(\delta_n, t)$ in figure 2 is thus equal to 0.

Combined to equation (8) and limit conditions (9) (J^{Li} being equal to 0 inside the separator), this assumption induces that the potential of the electrolyte along the separator is also constant:

$$\phi_e(x,t) = Cst \qquad \forall x \in [\delta_n, \delta_p].$$ (18)

According to assumption H_1 in (Sabatier et al, 2014), it is supposed that electrolyte potentials are constant in the two electrodes:

$$\phi_e(x \in [0, \delta_n[, t) = \phi_{en\_mean} \,,$$

and (19)

$$\phi_e \ (x \in]\delta_p L], t) = \phi_{ep\_mean} \,.$$

Thus assumption H_5 leads to:

$$\phi_{en\_mean} = \phi_{ep\_mean} \,.$$ (20)

Equation (20) shows that the lithium concentration information inside the electrolyte is no more necessary and the corresponding part in figure 2 can thus be suppressed.

Figure 3 : *Concentration (a) and potential (b) variations in the electrolyte during the first 60 seconds for a discharge current*

of 100A

Moreover, as shown in figure 3, the electrolyte potential changes very little regardless of the input current or battery state of charge, and remains close to $\phi_e \approx -0.1$ volts. It is therefore possible to make another simplifying assumption.

Assumption H_6

It is supposed that the electrolyte potential is constant at any SOC and such as:

$$\phi_e(x, Soc) = \phi_{e\_moy} = -0.1V \ . \tag{21}$$

Using this last hypothesis, the part of figure 2 model that represents the negative electrode contribution can be removed. The resulting model is a single-electrode model represented in figure 4. This model is obtained by moving and consolidating some blocks and by introducing the following parameters:

$$\begin{cases} K_1 = \dfrac{K}{A\delta_p c_{s\max p}} \ \ \text{with} \ \ \ K = \dfrac{-3}{R_s F a_s} = \dfrac{1}{F\varepsilon_s} \\ K_2 = \dfrac{RT}{A\delta_p F(\alpha_a + \alpha_c)a_{sp}i_{0p}} + R_f \\ \omega_{csp,e} = \dfrac{9D_{sp}}{R_s{}^2} \end{cases} \ . \tag{22}$$

IV. PARAMETERS ESTIMATION

According to the hypothesis previously done, only three parameters and a non-linear law are required to model the behavior of a lithium-ion cell. It is now described how the numerical values of these parameters can be obtained with the unique test of figure 5. This test consists in a series of discharges of 0.5 A.h since full charge (a decrease of around 7.1% on the SOC for each discharge from 100%). The interval between two discharges is large enough to permit a measure of the open loop circuit voltage. The parameters estimation method presented in the sequel is repeated for several state of charge and several temperatures to check the dependence of the parameters to these two variables.

Figure 4 - Single-electrode model

4.1 – Open circuit voltage law identification

We suppose that the open circuit voltage can be described by the relation proposed in (Karthikeyan et al, 2008):

$$U_p = U_p^0 + \frac{RT}{F} \ln\left(\frac{1 - \left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right)}{\left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right)} \right) + \left\{ \sum_{k=0}^{N_p} B_k \left[\frac{\left(2\left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right) - 1\right)^{k+1}}{-\frac{2\left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right)k\left(1 - \left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right)\right)}{\left(2\left(Soc\left(x_{100p} - x_{0p}\right) + x_{0p}\right) - 1\right)^{1-k}}} \right] \right\}. \tag{23}$$

Parameters B_k, x_{100p}, x_{0p} and U_p^0 associated to relation (23) are respectively and for the positive electrode, the interaction parameter in Redlich-Kister equation, lithium insertion ratios at SOC 100% and 0%, the standard equilibrium potential. These parameters are obtained through the minimization of a quadratic criterion on the open circuit voltage measured on figure 5. For that, the open circuit voltage is measured at rest (3600 s without any solicitation) after each current step that appears on figure 5. The variations of the open circuit voltage in relation to SOC are thus obtained and the corresponding curve is fitted by relation (23) through the minimization of a quadratic criterion.

4.2 – Estimation of parameter K_2

Parameter K_2 models the instant resistance due to contact resistance and to activation phenomenon inside the electrodes. As s tends towards infinity, namely as time tends towards 0, model in figure 4 reduce to $U(p) = K_2 I(p) + U_0/p$ (U_0 being the open circuit voltage of the cell), As a consequence and as shown in figure 6, if a constant current is applied to the cell, a voltage drop whose magnitude is liked to parameter K_2 appears. This is why figure 6 shows that this parameter can estimated on the cell voltage drop as a constant current is applied. K_2 is defined as the ratio of the voltage drop by the value of the current applied.

Figure 5 – *Discharge test for parameters numerical values estimation of the single-electrode model (only the first discharges are shown on this figure)*

Figure 6 – *Cell response to a step current and definitions of areas used for the identification of parameters K_1, K_2 and $\omega_{csp,e}$*

4.3 – Estimation of parameter K_1

If $I(t)$ is a current step of amplitude A_{mp}, then Laplace transform of $Y(t)$ signal (see figure 4) is defined by:

$$Soc(s) = \frac{K_1}{s}\left(1 + \frac{s}{\omega_{ce_p}}\right)^{0.5}\frac{A_{mp}}{s}. \tag{24}$$

Final value theorem applied to the derivative of Soc(t), leads to

$$\lim_{t \to +\infty} \frac{d(Y(t))}{dt} = \lim_{s \to 0} s^2 \frac{K_1}{s}\left(1 + \frac{s}{\omega_{ce_p}}\right)^{0.5} \frac{A_{mp}}{s} = K_1 A_{mp}. \tag{25}$$

Relation (25) means that after some time characterized by the time constant $1/\omega_{csp,e}$, (namely in the area in black in figure 6), if a constant current is applied to the cell, diffusion rate of Li^+ ions in the solid phase becomes sufficiently constant. This results in a linear variation of the cell voltage if the input current is not too high to avoid too rapid SOC variation (the open circuit voltage law can thus be assimilated to a straight line). This linear variation appears in figure 6 and this is why this figure defines le linear part of the step response as the time interval on which parameter K_1 can be estimated. Parameter K_1 is thus the slope (divided by A_{mp}) of function $Y(t)$ on the interval shown in figure 6, as a current step is applied to the cell. Function $Y(t)$ can be estimated using the inverse of the open circuit voltage curve, parameter K_2, and signals $I(t)$ and $U(t)$ being known.

4.4 – Identification of parameter ω_{csep}

From figure 4 model, a variable $v(t)$ can be defined such that:

$$v(s) = K_1\left(1 + \frac{s}{\omega_{csp,e}}\right)^{0.5} I(s). \tag{26}$$

If $I(t)$ is a step current of magnitude A_{mp} relation (26) becomes

$$v(s) = \frac{K_1 A_{mp}}{\sqrt{\omega_{csp,e}}} \frac{s^{0.5}}{s - \omega_{csp,e}}. \tag{27}$$

This relation highlight that parameter of $\omega_{csp,e}$. is at the origin of curvature that appears on the step response of figure 6 (response of a first order system). Sensitivity of the step response to this parameter is thus very high in the curvature and this is why figure 6 shows that the parameter is estimated on the response curvature as now explained.

Let

$$x(s) = \frac{1}{s - \omega_{csp,e}}. \tag{28}$$

Using Rieman-Liouville definition of fractional derivative (Miller et Ross, 1993),

$$L\{D^\gamma x(\tau)\} = s^\gamma \bar{x}(s) - \sum_{k=0}^{n-1} s^k \left[D^{\gamma-k-1} x(\tau)\right]_{\tau=0}, \tag{29}$$

or still using [Miller et Ross, 1993]

$$D^{-0.5}\left(e^{\omega_{csp,e}\tau}\right)_{\tau=0} = \left.\frac{e^{\omega_{csp,e}\tau}\,erf\left(\left(\omega_{csp,e}\tau\right)^{0.5}\right)}{\omega_{csp,e}^{0.5}}\right|_{\tau=0} = 0\,. \tag{30}$$

Using (30), relation (29) becomes :

$$L^{-1}\left(V\left(s-\omega_{csp,e}\right)\right) = \frac{K_1 A_{mp}}{\sqrt{\omega_{csp,e}}}\left[D\left(D^{-0.5}\left(e^{\omega_{csp,e}t}\right)\right)\right]. \tag{31}$$

Given that $D^{-0.5}\left(e^{\omega_{csp,e}\tau}\right)_{\tau=0} = \dfrac{e^{\omega_{csp,e}\tau}\,erf\left(\left(\omega_{csp,e}\tau\right)^{0.5}\right)}{\omega_{csp,e}^{0.5}}$,

$$L^{-1}\left(V\left(s-\omega_{csp,e}\right)\right) = \frac{K_1 A_{mp}}{\omega_{csp,e}}\left[\begin{array}{c} \omega_{csp,e}e^{\omega_{csp,e}t}\,erf\left(\left(\omega_{csp,e}t\right)^{0.5}\right) \\ + \dfrac{\omega_{csp,e}}{\sqrt{\pi}\left(\omega_{csp,e}t\right)^{0.5}} \end{array}\right]. \tag{32}$$

Using the following Laplace transform property:

$$L^{-1}\left(F(s)\right) = f(t) \;\Rightarrow\; L^{-1}\left(F(s+a)\right) = e^{-at}f(t), \tag{33}$$

then

$$L^{-1}\left(V\left(s-\omega_{csp,e}\right)\right) = e^{\omega_{csp,e}t}L^{-1}\left(v(s)\right), \tag{34}$$

and thus

$$v(t) = K_1 A_{mp}\left[erf\left(\left(\omega_{csp,e}t\right)^{0.5}\right) + \frac{e^{-\omega_{csp,e}t}}{\sqrt{\pi}\left(\omega_{csp,e}t\right)^{0.5}}\right]. \tag{35}$$

As $w(t) = \int v(t)dt$, then

$$w(t) = \frac{K_1 A_{mp}}{\omega_{csp,e}}\left(\begin{array}{c} 0.5erf\left(\left(\omega_{csp,e}t\right)^{0.5}\right) \\ + t\omega_{csp,e}erf\left(\left(\omega_{csp,e}t\right)^{0.5}\right) + \dfrac{0.5642\left(\omega_{csp,e}t\right)}{e^{\omega_{csp,e}t}} \end{array}\right). \tag{36}$$

As shown by figure 4, signal $w(t)$ can be obtained using $U(t)$, parameter K_2, c_{sp0} and the open circuit law been supposed known. Thus, if a t_0 is chosen such that:

$$t_0 = \frac{k}{\omega_{csp,e}} \quad \text{with} \quad k \in \mathrm{R}^+, \tag{37}$$

k being chosen such that at time t_0 the batteries state of charge is close to its initial value and in the time interval on which the step response curvature appears (see figure 6), Thus given that the function $z(t) = w(t)/t$ at $t=t_0$ is:

$$z(t_0) = \frac{K_1 A_{mp}}{k} \left(\begin{array}{c} 0.5 erf\left(\left(\frac{1}{k}\right)^{0.5}\right) \\ + \frac{1}{k} erf\left(\left(\frac{1}{k}\right)^{0.5}\right) + \frac{0.5642\left(\frac{1}{k}\right)}{e^{\frac{1}{k}}} \end{array} \right), \tag{38}$$

by searching this particular value of the function $z(t)$, the value of t_0 can be obtained and thus using (37), the value of $\omega_{csp,e}$.

Figure 7 - ± 20A PBRS current applied to the cell

V. MODEL VALIDATION

To validate the single electrode model previously given an its associated parameters estimation method, the ± 20A PBRS (Pseudo Binary Random Sequence) current of figure 7 is applied to the model and to a 7Ah real lithium ion cell. At the beginning of the test, the cell state of charge was Soc=80% and the temperature was T=25°C. The battery response is represented by figure 8. A zoom of this figure is proposed in figure 9. The relative error between the cell voltage and the model response is also represented in figure 8. Analysis of figures 8 and 9 shows a very good accuracy of the model with a relative error less than 0.5%. The dynamic behavior of the battery is thus very well captured by the model when the state of charge varies little around its starting point.

Figure 8 - Voltage variations comparison with a ± 20A PBRS current for Soc=80% and T=25°C

Figure 9 - Voltage variations comparison with a ± 20A PBRS current for Soc=80% and T=25°C

Figure 10 – Current cycle

The following validation is performed on the discharge cycles of figure 10. During this cycle, state of charge cell varies form 80% to 20%.

Figure 11 shows a comparison of the voltage and of the model response. A zoom of this comparison is proposed in figure 12. The relative error between cell voltage and model response is also shown in figure 11. These figures show that the model is

very efficient (less than 1.5% error). When the state of charge is below 20%, error mean value increases but remains low (less than 1%).

Figure 11 – Cell voltage variations / model response comparison for a current cycle and relative error T=25°C

Figure 12 – Cell voltage variations / model response comparison for a current cycle at 25°C

To further analyze the reliability of the proposed model, additional tests have been done for a temperature of 50°C. Figure 11 shows the results obtained for one of these tests. This additional validation is performed on a charge cycle comparable to that of figure 10. During this cycle, state of charge cell varies form 20% to 80%. Figure 13 shows a comparison of the voltage and of the model response. A zoom of this comparison is proposed in figure 14. The relative error between cell voltage and model response is also shown in figure 13. These figures highlight the model accuracy with a relative error less than 1.5%.

Figure 13 – Cell voltage variations / model response comparison for a current cycle and relative error T=50°C

Figure 14 – Cell voltage variations / model response comparison for a current cycle at 50°C

For very low temperature, model of figure 4 no more permits to obtain satisfactory results. For a temperature equal to -10°C, the relative error obtained is close to 5%. Assumption A5 is in fact no more valid. The dynamical behavior of the lithium ions in the electrolyte must be taken into account. For that, the "separator" part of figure 2 model is introduced in figure 4 model. The model that must be used in very low temperature is thus represented in figure 15. The parameters associated to this model are now estimated numerically, through the minimization of a quadratic criterion on the error between the voltage response of the battery and the voltage response of the model.

Figure 15 - *Single-electrode plus separator model*

To validate this model, the ± 10A PRBS (Pseudo Random Binary Sequence) current (as those represented in figure 7) is applied to the model and to a 7Ah real lithium ion cell at a temperature equal to -10°C. At the beginning of the test, the cell state of charge was Soc=80%. Figure 16 shows a comparison of the voltage and of the model response. A zoom of this comparison is proposed in figure 17. The relative error between cell voltage and model response is also shown in figure 16. These figures highlight that the model accuracy (less than 1.5% error) in spite of the very low temperature.

Figure 16 – Cell voltage variations / model response comparison for a PRBS type current cycle and relative error T=-10°C

Figure 17 – Cell voltage variations / model response comparison for a current cycle at -10°C

VI. CONCLUSION AND FUTURE WORK

In this paper a model for lithium-ion batteries has been proposed. It stems from several assumptions and simplifications made from an electrochemical model of the battery that involves several partial differential equations. Some have been resolved (solution of diffusion equation (2)) and this brings up a fractional transfer function. A simple model (low number of parameters in comparison with, for instance, an approach based on Padé approximation that leads to an integer model with a large number of parameters) has been obtained with such an approach. In this model, only 3 parameters must be estimated, and the open circuit voltage must be fitted by a polynomial. A very simple test consisting in a series of discharges separated by relaxation periods permits the parameters estimation and the polynomial fitting. Several validation tests (Merveillaut, 2011) (not presented here due to the limited number of pages) under various conditions (state of charge, temperature, current values and sign) have permitted to highlight that the obtained model permits to simulate the battery voltage with a relative error close to 0.5 %. Beyond the accuracy, another advantage of the proposed model is the low amount of resources required for an implementation in a car microcontroller of model in figure 4. In (Cugnet et al, 2009), some of the authors have experienced the implementation of an electrochemical model. Such an implementation requires the discretization in time and in space of the partial differential equations and of the limit conditions. The problem resolution then leads to the inversion and product of very large matrices (which is really resources consuming). Conversely, the implementation of a model such as in figure 4, can be done using a recurrence relation (after approximation of the fractional part using a distribution of poles and zeros and discretization) involving a low number of products and sum at each iteration. Thus the implementation of model in figure 4 is really less resources consuming than the electrochemical model.

In future papers, the authors will present additional tests on the presented single-electrode model and will use the proposed model to estimate battery state of charge and available power. These works on lithium-ion modelling and monitoring take place in the open lab "Electronics and Systems for Automotive" combining IMS laboratory and PSA Peugeot Citroën society.

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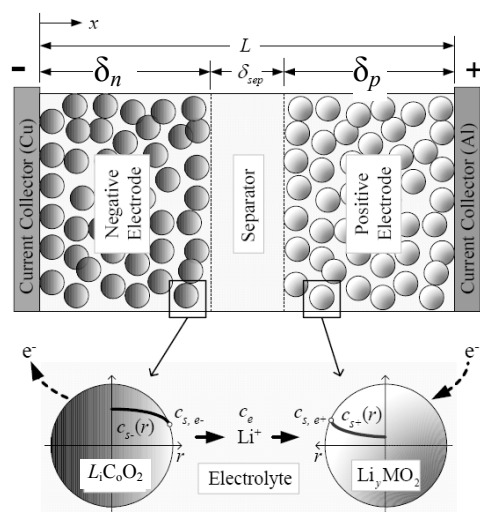
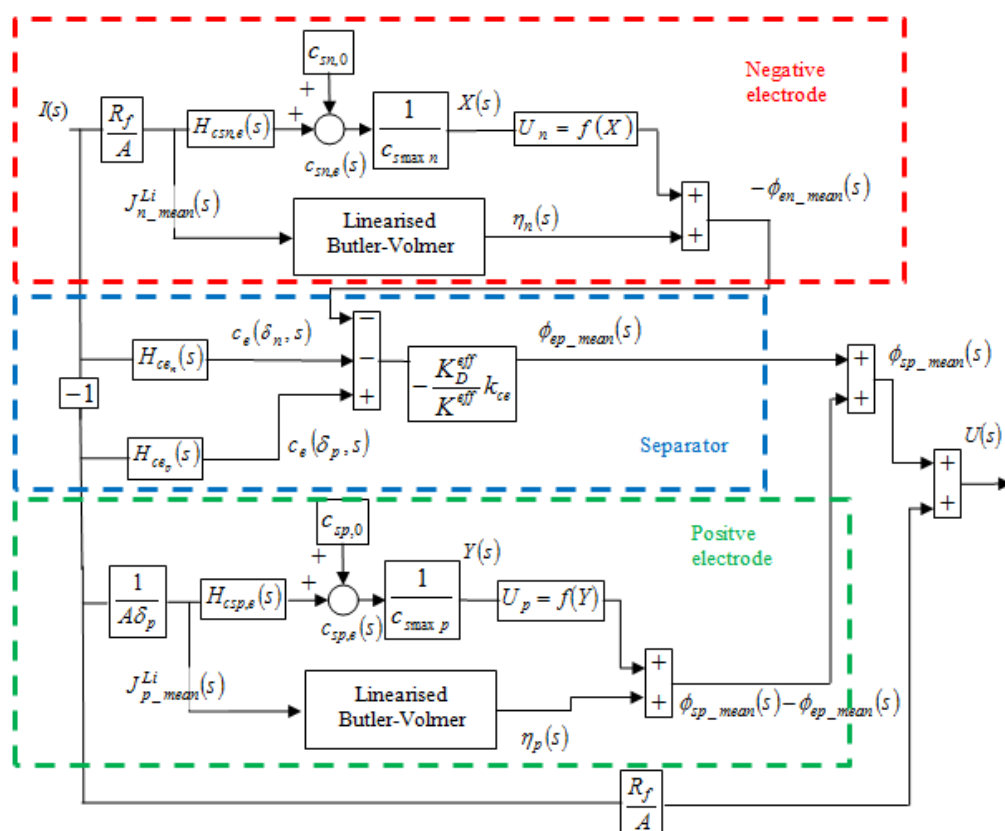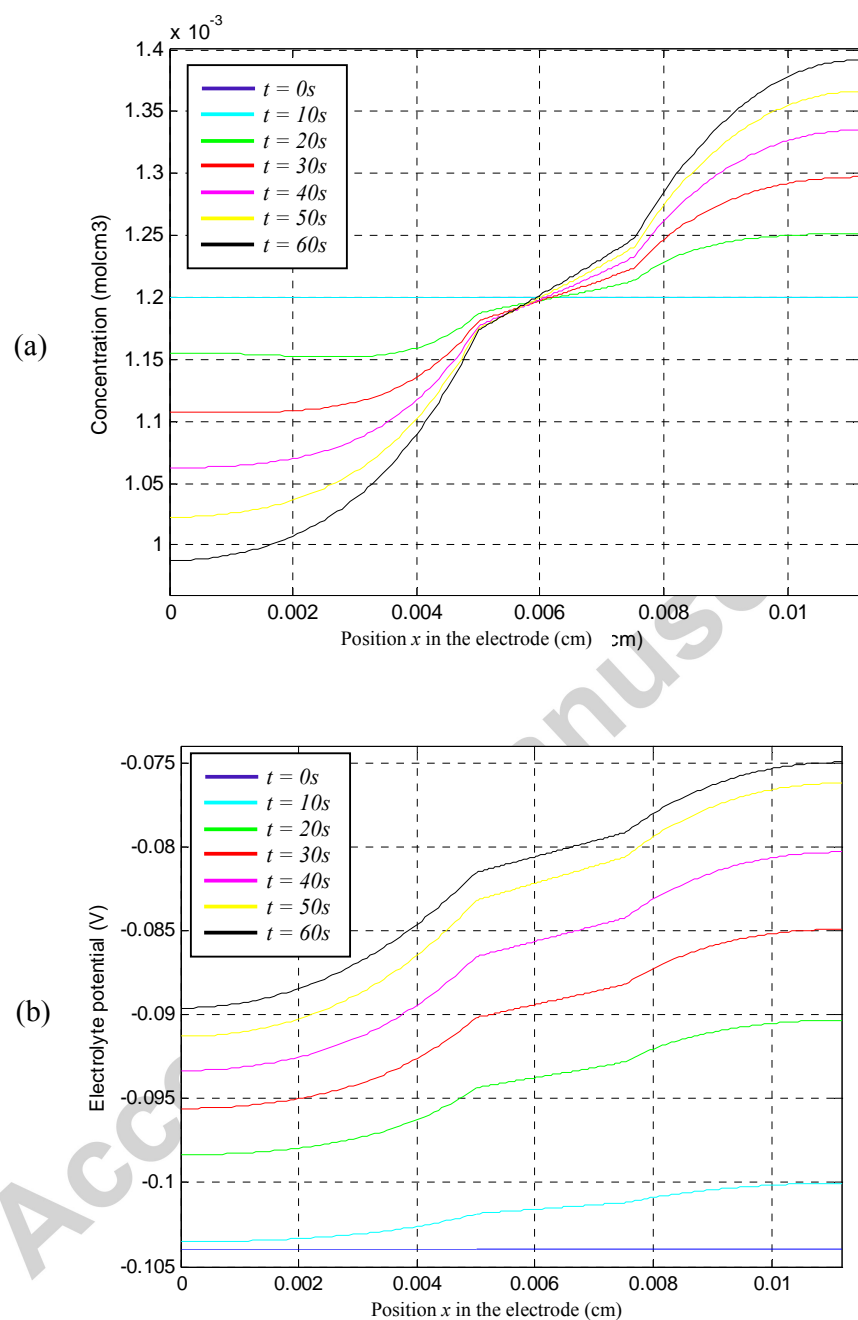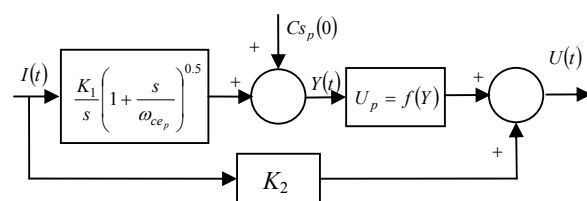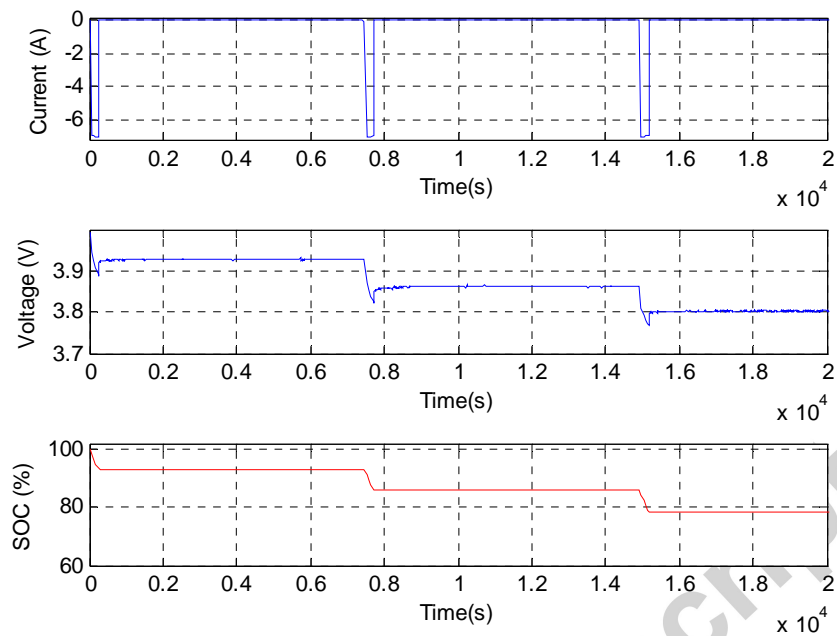***Figure 1 -*** *Pseudo 2D model of a lithium-ion cell*

(Smith et al, 2010)

Figure 2 : *First simplified model obtained*

(a)

(b)

Figure 3 : *Concentration (a) and potential (b) variations in the electrolyte during the first 60 seconds for a discharge current*

of 100A

$$I(t) \rightarrow \boxed{\frac{K_1}{s}\left(1+\frac{s}{\omega_{ce_p}}\right)^{0.5}} \xrightarrow{+} \bigcirc \xrightarrow{Y(t)} \boxed{U_p = f(Y)} \xrightarrow{+} \bigcirc \rightarrow U(t)$$

$Cs_p(0)$

$\boxed{K_2}$

Figure 4 - *Single-electrode model*

Figure 5 *– Discharge test for parameters numerical values estimation of the single-electrode model (only the first discharges*

are shown on this figure)
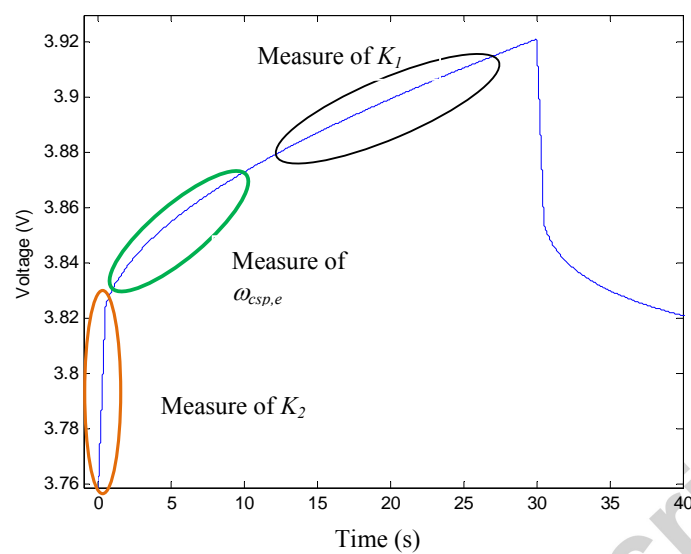
Figure 6 – *Cell response to a step current and definitions of areas used for the identification of parameters K_1, K_2 and $\omega_{csp,e}$*
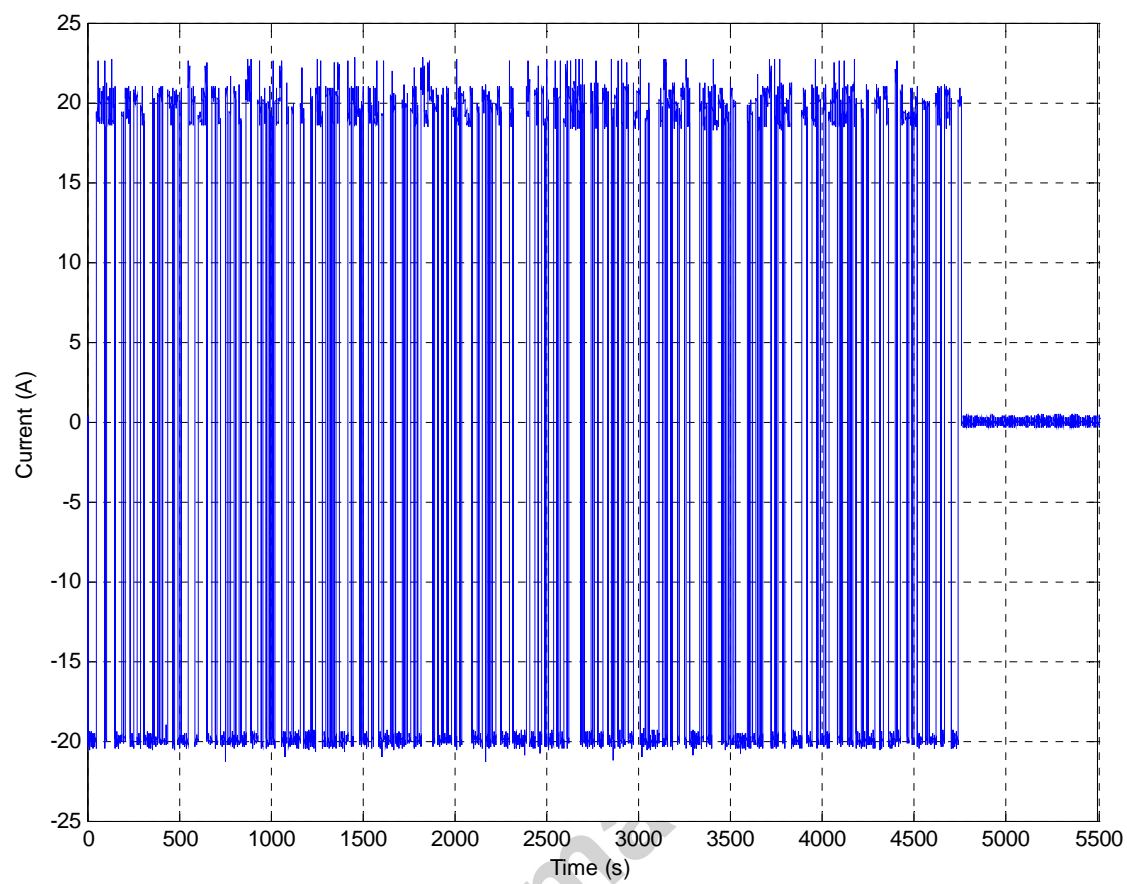
Figure 7 - ± 20A PBRS current applied to the cell
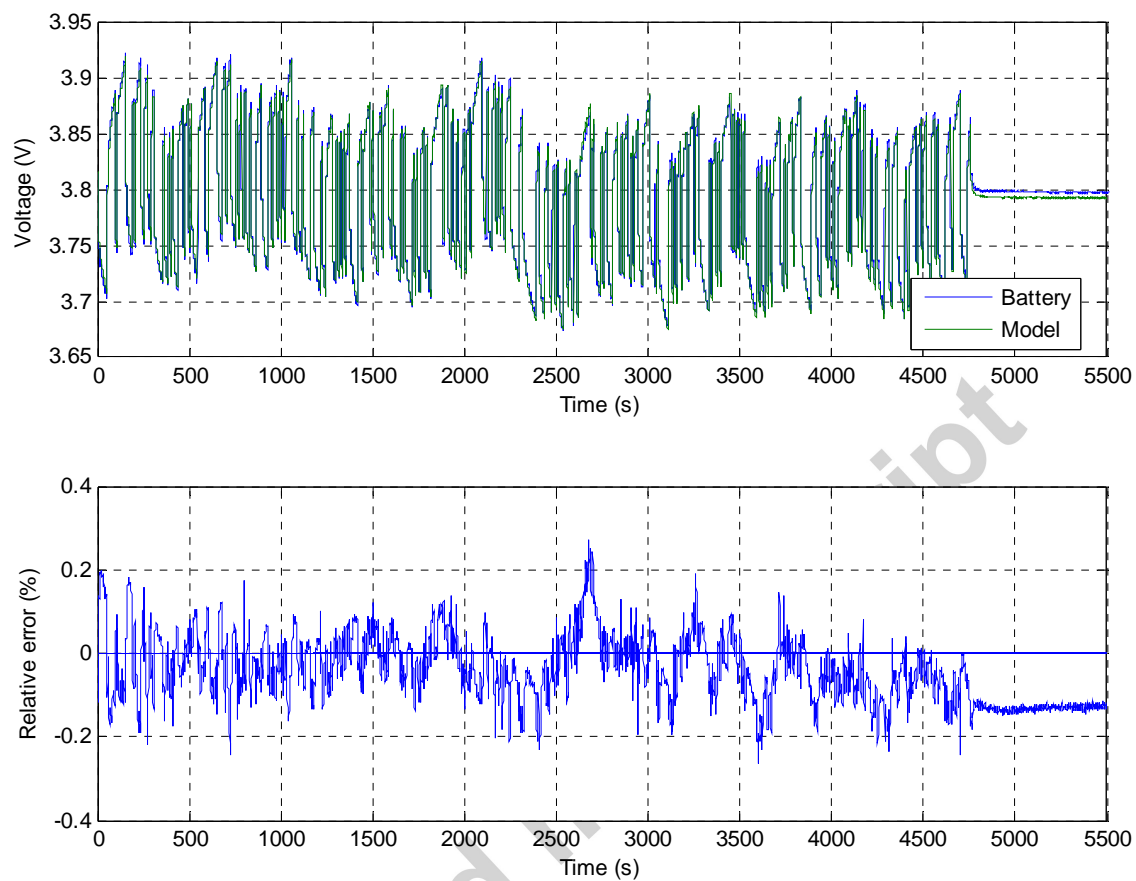
Figure 8 - Voltage variations comparison with a ± 20A PBRS current for Soc=80% and T=25°C
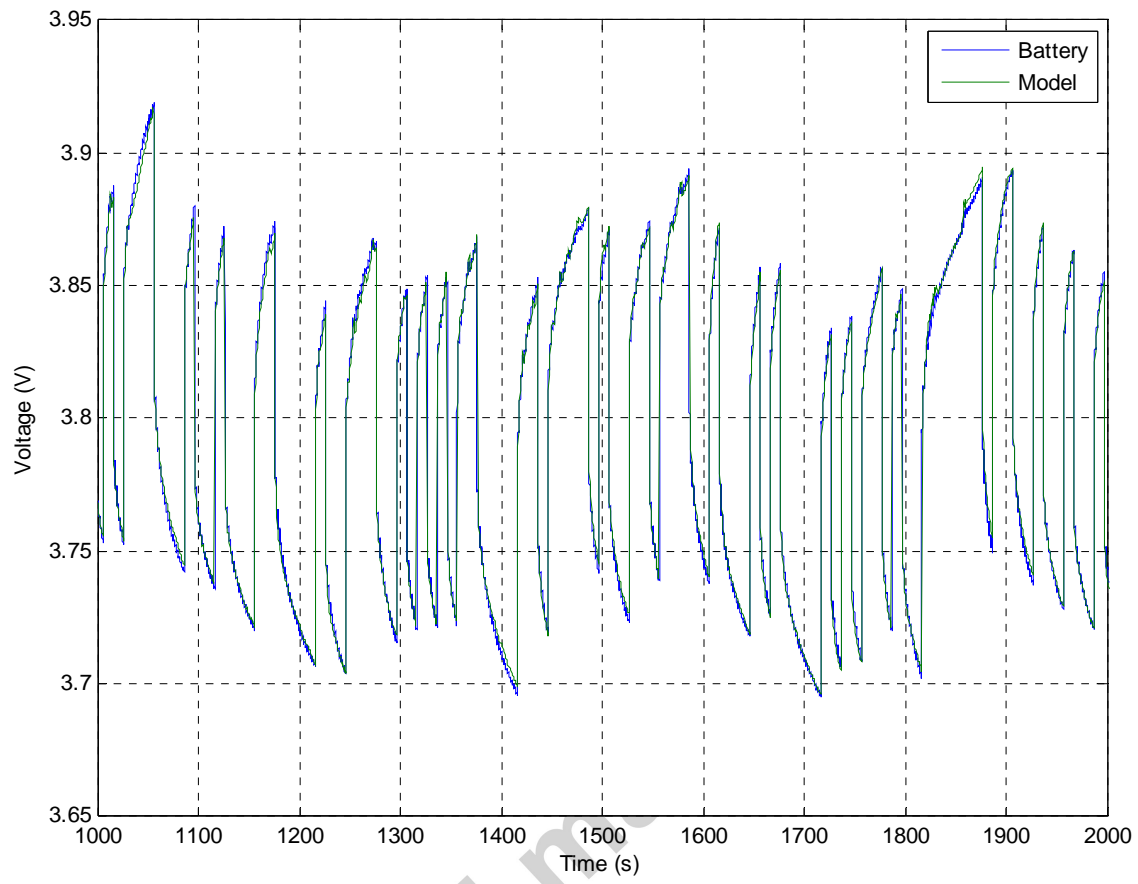
Figure 9 - Voltage variation comparison with a ± 20A PBRS current for Soc=80% and T=25°C
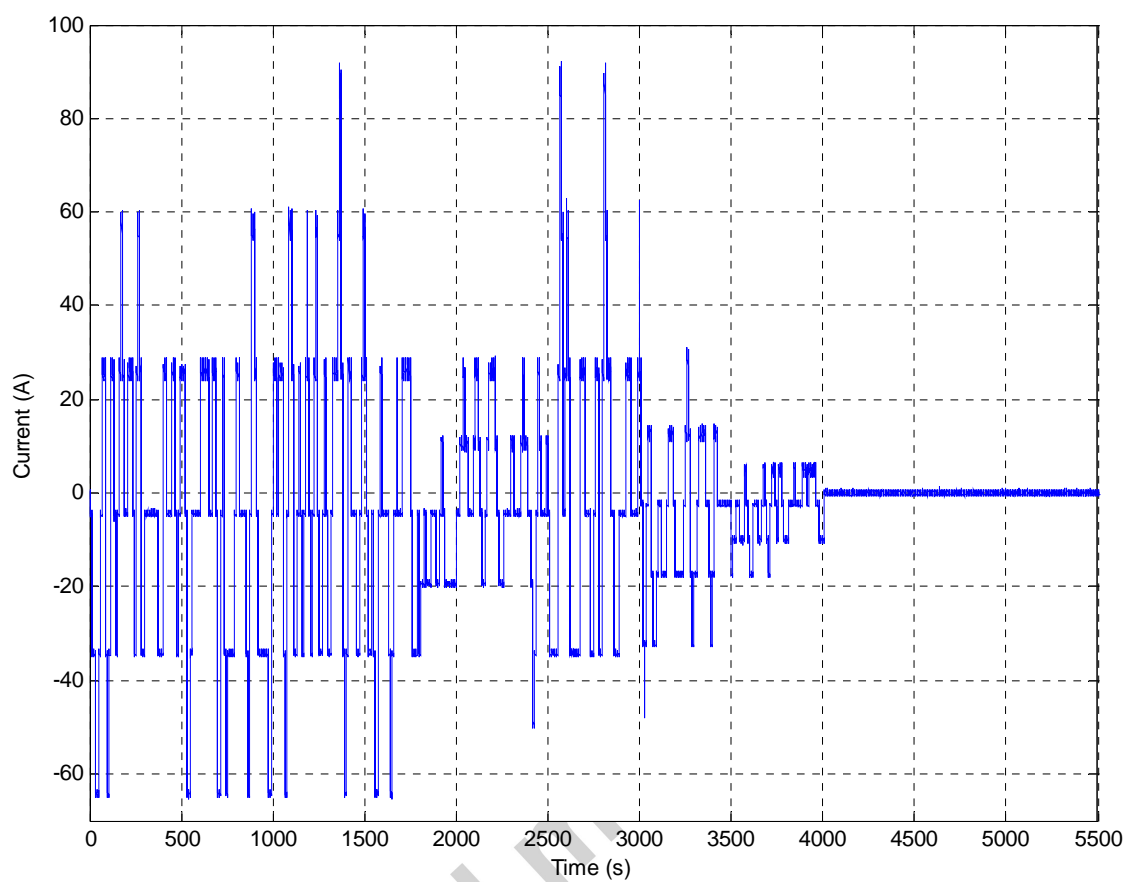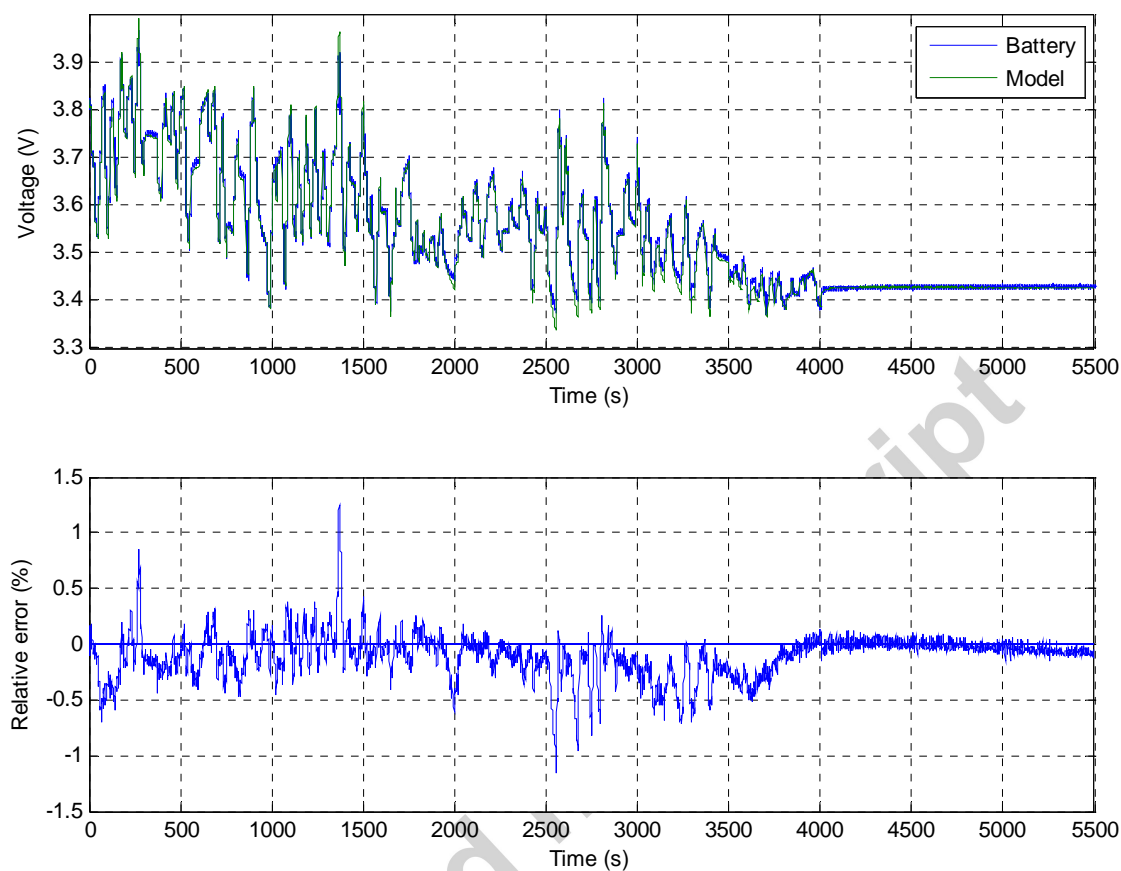
Figure 10 – Current cycle

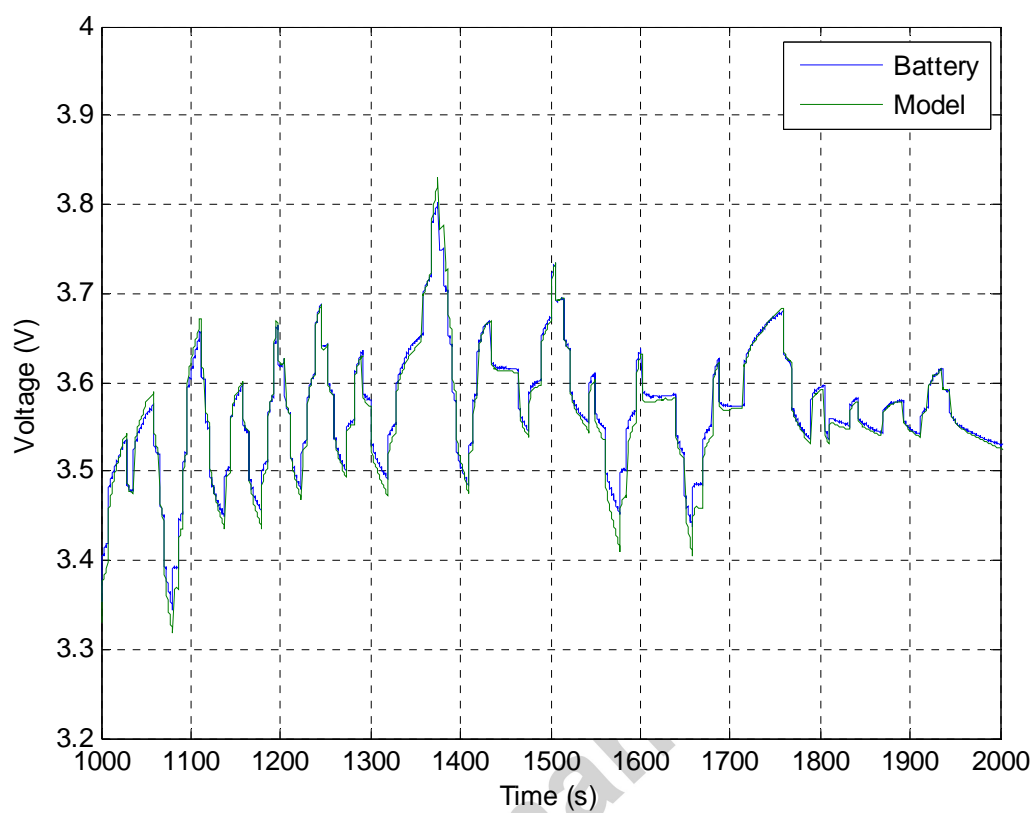*Figure 11 – Cell voltage variations / model response comparison for a current cycle and relative error T=25°C*
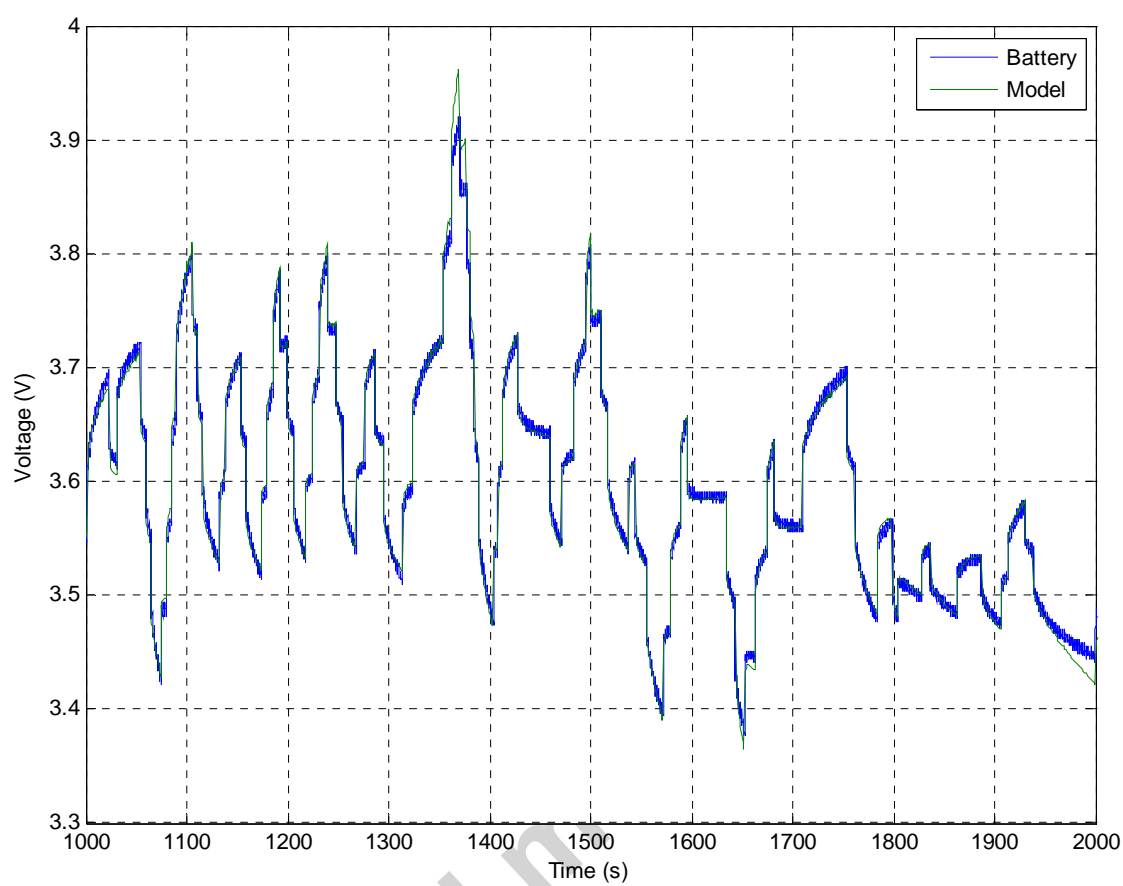
Figure 12 – Cell voltage variations / model response comparison for a current cycle at 25°C
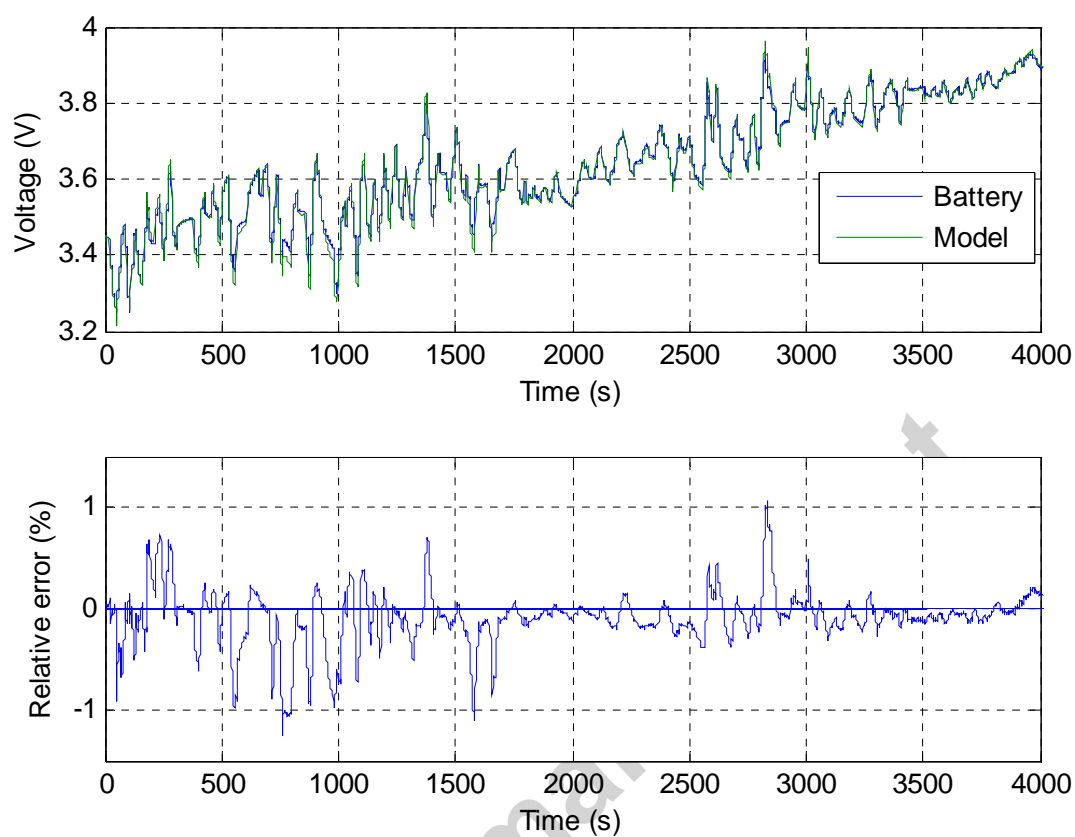
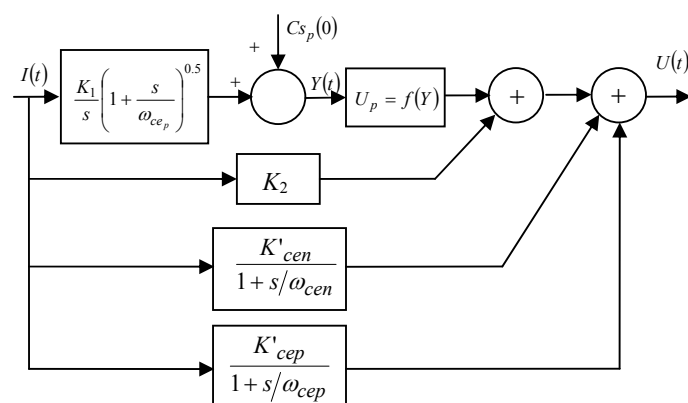*Figure 13 – Cell voltage variations / model response comparison for a current cycle and relative error T=50°C*

Figure 14 – Cell voltage variations / model response comparison for a current cycle at 50°C
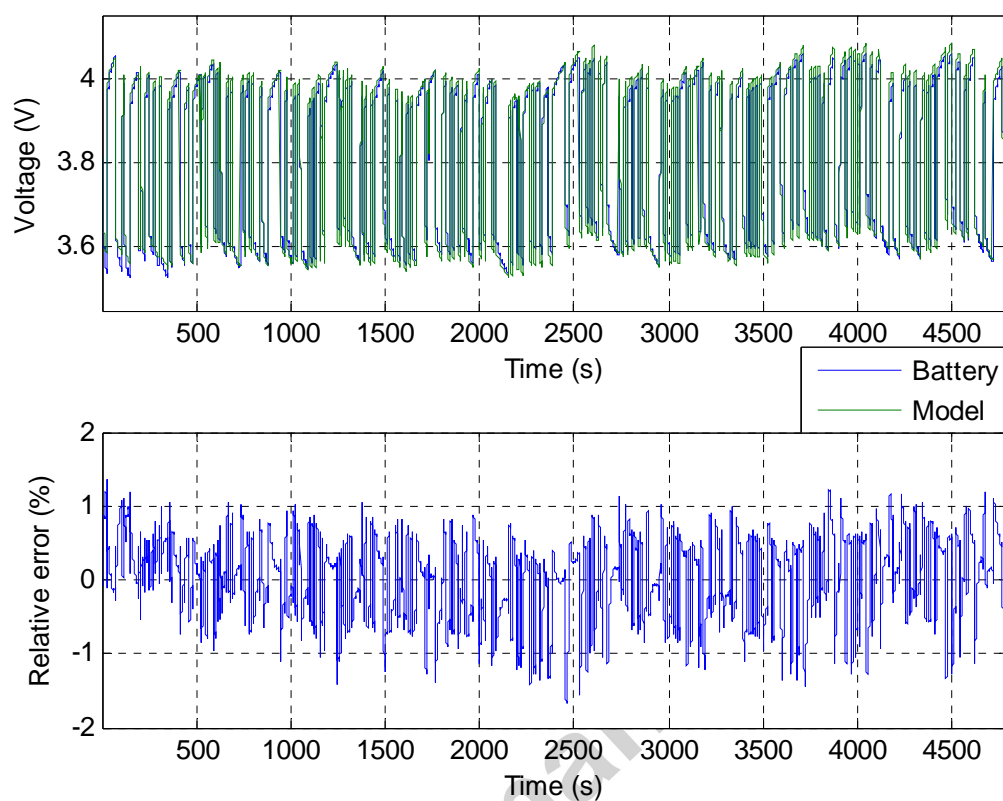
Figure 15 - *Single-electrode plus separator model*

Figure 16 – Cell voltage variations / model response comparison for a PRBS type current cycle and relative error T=-10°C
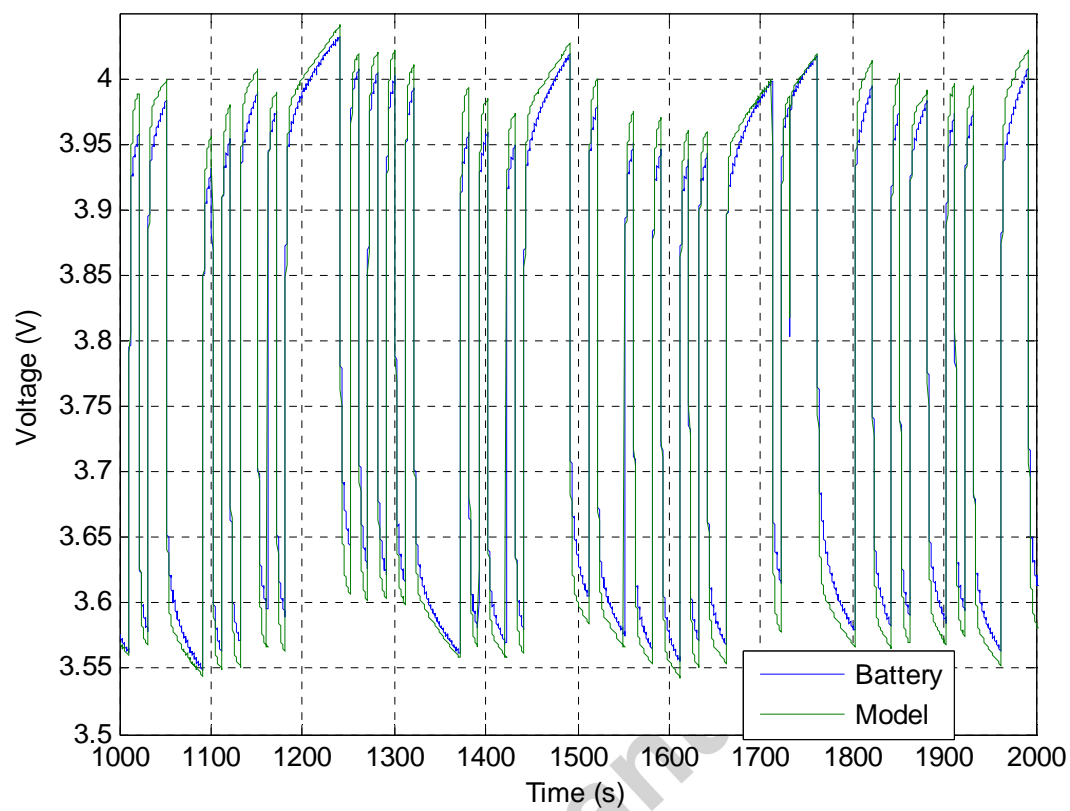
Figure 17 – Cell voltage variations / model response comparison for a current cycle at 50°C

- battery electrochemical model.
-
- parameters in the model.
- obtained under various conditions
- use in automobile BMS.

A simplified model is obtained from a lithium-ion

The proposed model is a single-electrode model.

Fractional differentiation is used for a low number of

A relative error less than 0.5% on the voltage is

The model simplicity and accuracy are interesting for