

## Fractional models for lithium-ion batteries

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**Abstract** – With hybrid and electric vehicles development, automobile battery monitoring systems (BMS) have to meet the new requirements. These systems have to give information, on state of health, state of charge, available power. To get this information, BMS often implement battery models. Accuracy of the information manipulated by the BMS thus depends on the model accuracy. This paper is within this framework and addresses lithium-ion battery modeling. The proposed fractional model is based on simplifications of an electrochemical model and on resolution of some partial differential equations used in its description. Such an approach permits to get a simple model in which electrochemical variables and parameters still appear.

**Keywords** – Lithium-ion batteries, fractional models.

### I. INTRODUCTION

More and more drastic automobile pollution norms and oil price increase, lead car manufacturers to design new vehicles (stop and start, hybrid, or electric). The underlying idea is to reduce exhaust emissions in the built-up areas, either by stopping the internal combustion engine when the vehicle is not moving, or by substituting electric fuel for fossil fuel. The latter may involve an electric motor and one or more energy storage system. To keep these new vehicles in good working order, car manufacturers must integrate a reliable electrical energy storage management (Chatzakis, 2003). That is why, state of charge (SOC) and state of health (SOH) estimators must be designed. To design these estimators, dynamical models of the battery pack can be a valuable tool

In this paper, a dynamical model of a lithium-ion battery is proposed. Many models exist in the literature for this kind of batteries such as purely eclectic models (Buller, 2005) or fuzzy models (Sinh et al, 2006). An extensive analysis on lithium ion batteries modeling is proposed in (Sikha et al, 2005). The originality here is the way this model is obtained. It results from simplification of an electrochemical model that describes the battery behavior using partial differential equations. Interest of this approach is that it is possible to link the electrochemical parameters of the battery to the resulting dynamic model parameters. This model has thus an important physical meaning, unlike purely electric models proposed in the literature. Another interest is the introduction of fractional differentiation that helps to describe some parts of the model with a small number of parameters again directly related to the electrochemical parameters of the battery. Such a model can then be used to design SOC or SOH estimators.

### II. ELECTROCHEMICAL MODEL

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

In figure 1, the electrodes are seen as an aggregation of spherical particles (2D representation) in which the  $\text{Li}^+$  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.

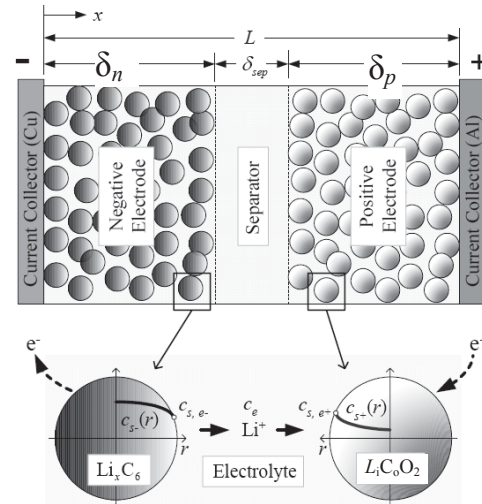


Figure 1 - Pseudo 2D model of a Lithium-ion cell (Smith et al, 2010)

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

- $x = 0$  : negative electrode current collector ;
- $x \in ]0; \delta_n[$  : region 1,  $\delta_n$  thickness negative carbon electrode ( $\text{Li}_x\text{C}_6$ , MCMB...);
- $x = \delta_n$  : negative electrode / separator interface;
- $x \in ]\delta_n; \delta_n + \delta_{sep}[$  : region 2,  $\delta_{sep}$  thickness separator;
- $x = \delta_n + \delta_{sep}$  : separator / positive electrode interface;
- $x \in ]\delta_n + \delta_{sep}; L[$  : region 3,  $\delta_p$  thickness positive electrode made of  $\text{LiCoO}_2$ ;
- $x = L$  : 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  $U_{bat}(t)$  is defined by the relation

$$U_{batt}(t) = \phi_s(L, t) - \phi_s(0, t) - \frac{R_f}{A} I(t) \quad (1)$$

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 resistance and  $A$  the electrodes surface. Note that all the parameters used in the following equation are defined in (Smith, 2006) (Smith et al, 2010).

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

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

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

$$\frac{\partial(\epsilon_e c_e)}{\partial t} = \frac{\partial}{\partial x} \left( D_e^{eff} \frac{\partial c_e}{\partial x} \right) + \frac{1-t_+^0}{F} j^{Li}, \quad (3)$$

with

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

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

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

with the following limit conditions at the current collectors

$$-\sigma_-^{eff} \left. \frac{\partial \phi_s}{\partial x} \right|_{x=0} = \sigma_+^{eff} \left. \frac{\partial \phi_s}{\partial x} \right|_{x=L} = \frac{I}{A}, \quad (6)$$

and the null current conditions at the separator:

$$\left. \frac{\partial \phi_s}{\partial x} \right|_{x=\delta_n} = \left. \frac{\partial \phi_s}{\partial x} \right|_{x=\delta_n+\delta_{sep}} = 0. \quad (7)$$

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

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

with the limit conditions

$$\left. \frac{\partial \phi_e}{\partial x} \right|_{x=0} = \left. \frac{\partial \phi_e}{\partial x} \right|_{x=L} = 0. \quad (9)$$

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

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

In (10),  $j^{Li}$  is induced by overvoltage  $\eta$ , defined by the potential difference between the solid phase and the electrolyte and equilibrium thermodynamic potential  $U$ :

$$\eta = \phi_s - \phi_e - U. \quad (11)$$

The equilibrium potential  $U$  is a function of the solid phase concentration at the spherical particle.

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 DYNAMIC MODEL

The electrochemical model previously describes has been implemented under Comsol Multiphysics and its parameters have been adjusted to fit a SAFT VL7P battery behavior. This model was then used to speculate assumptions now presented.

#### 3.1. Assumptions

- Assumption  $H_1$

It is supposed that electrolyte and solid phase potentials are constants in the two electrodes:

$$\begin{cases} \phi_s(x, t) = \phi_{s\_moy}(t) \\ \phi_e(x, t) = \phi_{e\_moy}(t) \end{cases} \quad (12)$$

Moreover, negative electrode is supposed connected to the ground. Negative electrode solid phase potential is thus null.

$$\phi_{sn}(t) = \phi_s(x, t) = \phi_{s\_moy}(t) = 0 \quad \forall x \in [0, \delta_n]. \quad (13)$$

To validate assumption H1, the current profile of figure 2 is applied to the electrochemical model. The resulting potentials are represented by figure 3.

- Assumption  $H_2$

Current density  $j^{Li}$  is supposed constant in each electrode. It is moreover supposed equal to its mean value for a given electrode:

$$j_i^{Li}(t) = j_{i\_mean}^{Li}(t) = \frac{\Delta}{\delta_i} \int_0^{\delta_i} j^{Li}(t, x) dx \quad (14)$$

with  $i = n, p$  ( $n$  = negative electrode,  $p$  = positive electrode).

For current in figure 2, figure 4 shows the current density  $j^{Li}(t)$  in the 2 electrodes and validates assumption  $H_2$  for the positive electrode. Due to the low impact of the negative electrode on the whole cell behavior (this electrode only create small voltage variations, ageing been not modeled here), assumption H2 is also supposed valid for this electrode.

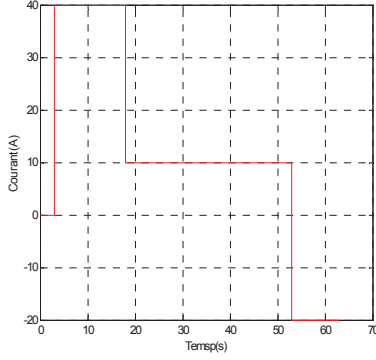


Figure 2 Current profile used to validate assumption  $H_1$

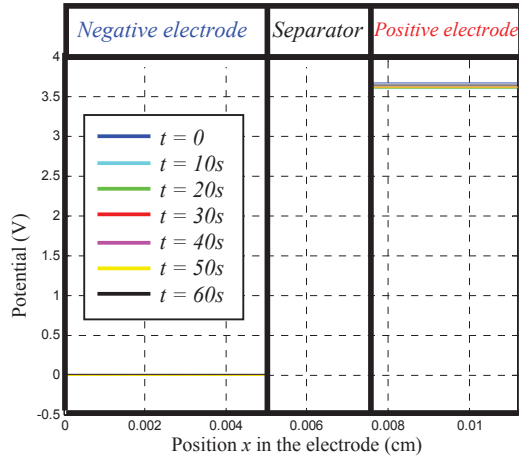


Figure 3 : Solid phase potential in all the cell

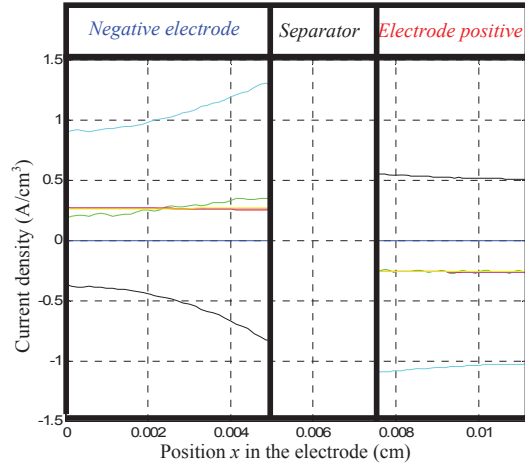


Figure 4 : Current density  $j^{Li}$  in the electrodes

Equation (5) integration for negative electrode leads to:

$$\sigma_{eff} \left[ \left( \frac{\partial}{\partial x} \phi_s(t, x) \right) \Big|_{x=\delta_n} - \left( \frac{\partial}{\partial x} \phi_s(t, x) \right) \Big|_{x=0} \right] = \int_0^{\delta_n} j_n^{Li}(t, x) dx \quad (15)$$

or given equations (6) and (7)

$$\frac{I(t)}{A} = \int_0^{\delta_n} j_n^{Li}(t, x) dx \quad (16)$$

and thus given assumption  $H_2$  and for the two electrodes

$$j_{i\_mean}^{Li}(t) = \frac{I(t)}{A\delta_i} = j_i^{Li}(t) \quad i = n, p. \quad (17)$$

- Assumption  $H_3$

Butler-Volmer equation defined by

$$j_i^{Li}(t) = a_{si} i_{0i} \left\{ \exp\left(\frac{\alpha_a F}{RT} \eta_i(t)\right) - \exp\left(-\frac{\alpha_c F}{RT} \eta_i(t)\right) \right\}, \quad (18)$$

with

$$\eta_i(t) = \phi_{si}(t) - \phi_{ei}(t) - U_i(t). \quad (19)$$

is supposed linear on the current range defined by table in figure 5 for a SAFT VL7P battery.

	VL7 P	VL20 P	VL30 P
<b>Electrical characteristics</b>			
Nominal voltage [V]	3,6	3,6	3,6
Average capacity 1C after charge to 4.0 V/cell [Ah]	7	20	30
Minimum capacity 1C after charge to 4.0 V/cell [Ah]	6,5	18,5	28
Specific energy after charge to 4.0 V/cell [Wh/kg]	67	89	97
Energy density after charge to 4.0 V/cell [Wh/dm <sup>3</sup> ]	131	187	209
Specific power [10s/50% DOD] [W/kg]	1811	1413	1136
Power density [10s/50% DOD] [W/dm <sup>3</sup> ]	3526	2974	2451
<b>Voltage limits</b>			
Charge [V]	4.0 (4.1 for peak)		
Discharge [V]	2.5 (2.0 for cold cranking)		
<b>Current limits</b>			
Max continuous current [A]	100	250	300
Max peak current during 10s [A]	250	500	500

Figure 5 : VLxP SAFT Batteries characteristics

This assumption is validated using the electrochemical model. Even with a high value current (a positive stroke followed by a negative one with 100A each),  $\eta_i$  variations remains close to 0 (see figure 6).

Using the first term of the Taylor expansion of the exponential function in relation (18), a linear approximation of this relation is thus:

$$j_{i\_mean}^{Li}(t) = a_{si} i_{0i} \left( \frac{\alpha_a F}{RT} \eta_i(t) + \frac{\alpha_c F}{RT} \eta_i(t) \right) \quad (20)$$

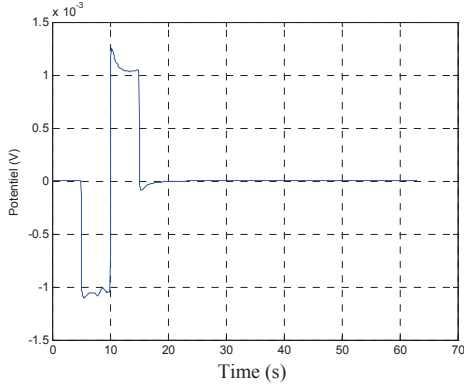
with  $\alpha_a + \alpha_c = 1$ . Using a simple graph, it is then easy to check that this approximation leads to an error less then 0.2 % for supply currents close to 250 A (maximal peak current).

Using equations (18) and (19), then:

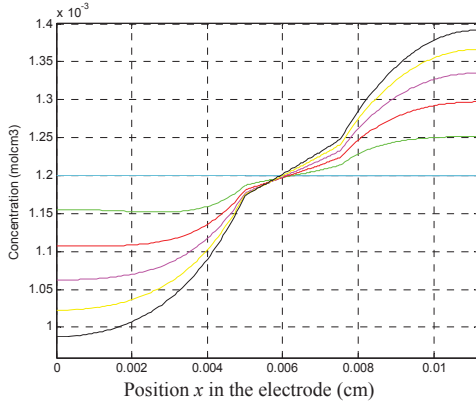
$$\phi_{ei}(t) = \phi_{si}(t) - U_i(t) - \frac{j_{i\_mean}^{Li}}{a_{si} i_{0i} F (\alpha_a + \alpha_c)}. \quad (21)$$

- Assumption  $H_4$

Lithium concentration in the separator is supposed a linear function of  $x$  around the initial value denoted  $C_e(x, 0)$ . This assumption is validated by figure 7.



**Figure 6 :**  $\eta_n$  and  $\eta_p$  overvoltage for the current profile of  $\pm 100A$



**Figure 7 :** Concentration variation in the electrolyte during the first 10 seconds

In the separator, equation (8) becomes

$$\frac{\partial}{\partial x} \left( \kappa^{eff} \frac{\partial \phi_{ei}(x,t)}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{\kappa_D^{eff}}{c_{ei}(x,t)} \frac{\partial}{\partial x} c_{ei}(x,t) \right) = 0 \quad (22)$$

or after integration,

$$\kappa^{eff} \frac{\partial}{\partial x} \phi_{ei}(x,t) + \frac{\kappa_D^{eff}}{c_{ei}(x,t)} \frac{\partial}{\partial x} c_{ei}(x,t) = C \quad (23)$$

Limit conditions (9) shows that constant  $C$  is equal to 0, and thus equation (23) becomes

$$\kappa^{eff} \frac{\partial}{\partial x} \phi_{ei}(x,t) + K_{ce} \kappa_D^{eff} \frac{\partial}{\partial x} c_{ei}(x,t) = 0 \quad (24)$$

with  $K_{ce} = 1/c_{ei}(x,0)$ .

Equation (24) links  $\phi_{ei}(x,t)$  to  $c_{ei}(x,t)$ . Using linearity assumption  $H_4$ , if one of these variables is known in all the cell, and if the second one is known on the positive or negative electrode, relation (24) permits to deduce this second variable on the remaining electrode.

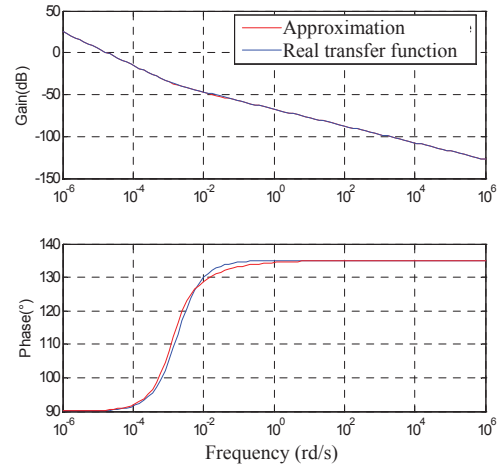
### 3.2. Model construction

Analytical solution of (4) leads to the transfer function that links  $c_{si,e} = c_{si}(p, r = R_s)$  to  $j_i^{Li}$ , given by:

$$H_{csi}(p, R_s) = H_{csi,e}(p) = \frac{c_{se,i}(p)}{j_i^{Li}(p)} = \frac{-R_s}{FD_{si} a_{si} \left( \sqrt{\frac{p}{D_{si}}} R_s \coth \left( \sqrt{\frac{p}{D_{si}}} R_s \right) - 1 \right)} \quad (25)$$

Due to *coth* function, relation (25) cannot be easily used for simulation or control purpose. A frequency approximation can be used to overcome this problem. Bode diagrams of  $H_{csn,e}(p)$  in figure 8 (but a similar one can be obtained for  $H_{csp,e}(p)$ ), indeed show that transfer functions  $H_{csi,e}(p)$  can be approximated using the fractional transfer function

$$H_{csi,e}^{app}(p) = \frac{K_{li} \left( 1 + \frac{p}{\omega_{csei}} \right)^{0.5}}{p} \quad (26)$$



**Figure 8 :**  $H_{csn,e}(p)$  and  $H_{csn,e}^{app}(p)$  Bode diagram comparison

Parameter  $K_{li}$  can be deduced from the Taylor expansion of (25). Gain  $K_{li}$  corresponds to the coefficient of the lowest degree term:

$$K_{li} = \frac{-3}{R_s F a_{si}} \quad (27)$$

Then to impose a similar high frequency behavior to (25) and to its approximation, a limit study lead to define the corner frequency  $\omega_{csei}$  by:

$$\omega_{csei} = \frac{9D_{si}}{R_s^2} \quad (28)$$

Figures 8 validates the approximation of transfer function  $H_{csn,e}(p)$  by  $H_{csn,e}^{app}(p)$ . A similar conclusion can be obtained with transfer function  $H_{csp,e}(p)$

$Li^+$  ionic current inside electrolyte is modeled by equation (3) with limit conditions (4). Laplace transform of equation (3) is given by:

$$p\varepsilon_e c_e - \lim_{t \rightarrow 0^+} c_e(t, x) = \frac{d}{dx} \left( D_e^{eff} \frac{d}{dx} c_e \right) + \frac{1-t_0^+}{F} j^{Li}. \quad (29)$$

Solution of this equation is thus:

$$c_e(p, x) = + \frac{(1-t_0^+)}{F} j_{mean}^{Li} + \frac{c_e(0, x)}{p\varepsilon_e} + C_3 \exp\left(\frac{\sqrt{p\varepsilon_e} \cdot 0.5(1-p)}{\sqrt{D_e}} x\right) + C_4 \exp\left(-\frac{\sqrt{p\varepsilon_e} \cdot 0.5(1-p)}{\sqrt{D_e}} x\right), \quad (30)$$

where  $c_e(0, x)$  denotes the initial concentration. A cell is made of 3 regions in which concentration variation is thus driven by three equations similar to (30). Thus the six constants  $C_{3n}$ ,  $C_{3s}$ ,  $C_{3p}$ ,  $C_{4n}$ ,  $C_{4s}$  and  $C_{4p}$  need to be computed using the following limit conditions

$$\left\{ \begin{array}{l} c_{en}(t, x = \delta^-) = c_{es}(t, x = \delta^-) \\ c_{en}(t, x = \delta^- + \delta^{sep}) = c_{ep}(t, x = \delta^- + \delta^{sep}) \\ \left. \frac{\partial c_{en}(t, x)}{\partial x} \right|_{x=0} = 0 \\ \left. \frac{\partial c_{ep}(t, x)}{\partial x} \right|_{x=L} = 0 \\ D_{en}\varepsilon_{en} p \left. \frac{\partial c_{en}(t, x)}{\partial x} \right|_{x=\delta_n} = D_{es}\varepsilon_{es} p \left. \frac{\partial c_{es}(t, x)}{\partial x} \right|_{x=\delta_n} \\ D_{es}\varepsilon_{es} p \left. \frac{\partial c_{es}(t, x)}{\partial x} \right|_{x=\delta_n + \delta_{sep}} = D_{ep}\varepsilon_{ep} p \left. \frac{\partial c_{ep}(t, x)}{\partial x} \right|_{x=\delta_n + \delta_{sep}} \end{array} \right. \quad (31)$$

The six constants depends on  $J_{i\_mean}^{Li}(t, x)$ , and thus due to relations (17) to the current  $I(t)$ . Transfer functions  $H_{esn}(p, x) = c_{en}(p, x)/I(p)$ ,  $H_{ces}(p, x) = c_{es}(p, x)/I(p)$  and  $H_{cep}(p, x) = c_{ep}(p, x)/I(p)$  can thus be deduced.

Bode diagrams of  $H_{cen}(p)$  in figure 9 (but similar ones are obtained for  $H_{cep}(p)$ ) shows that frequency response of this transfer function is similar to those of a first order system. It is thus possible to propose the following approximation:

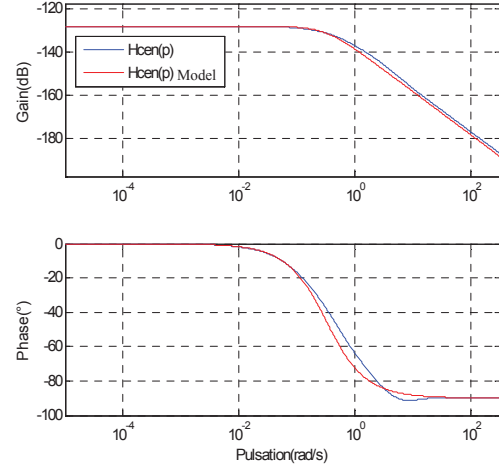
$$H_{cei}(p) = \frac{K_{cei}}{1 + \frac{p}{\omega_{cei}}}. \quad (32)$$

System identification applied on measures obtained with a 50 amperes current leads to the following parameters:

$$K_{cen} = 3.7736e^{-7} \text{ mol.cm}^{-3} \text{ and } \omega_{cen} = 10^{-0.493445} \text{ rad.s}^{-1}; \\ K_{cep} = -1.368e^{-6} \text{ mol.cm}^{-3} \text{ and } \omega_{cep} = 10^{-0.862} \text{ rad.s}^{-1}.$$

Contact resistance and also initial solid electrolyte interface can be taken into account by with the resistance  $R_f$  in the equation:

$$U_{batt}(p) = \phi_{sp}(L, t) - \frac{R_f}{A} I(p), \quad (33)$$



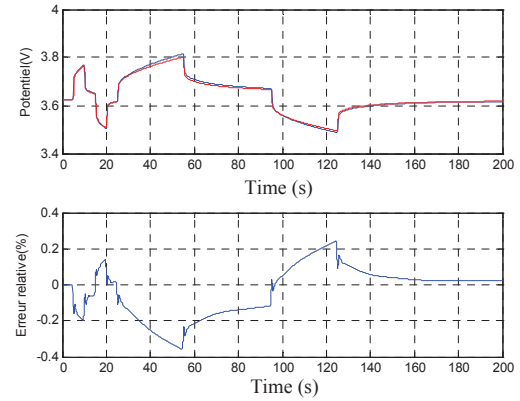
**Figure 9:** Bode diagram of transfer function  $H_{cen}(p)$  and its approximation

Finally, negative and positive electrodes equilibrium potentials are supposed defined by:

$$U_n(x) = 8.00229 + 5.0647z - 12.578z^{1/2} - 8.6322e^{-4}z^{-1} + 2.1765e^{-5}z^{3/2} - 0.46016 \exp[15.0(0.06 - z)] - 0.55364 \exp[-2.4326(z - 0.92)] \quad (34)$$

$$U_p(x) = 85.681y^6 - 357.70y^5 + 613.89y^4 - 555.65y^3 + 281.06y^2 - 76.648y - 0.30987 \exp(5.657y^{115.0}) + 13.1983 \quad (35)$$

where  $z$  and  $y$  denote respectively negative and positive electrode solid phase stoichiometries.



**Figure 11:** Model and battery voltage comparison and relative error at  $T=-10^\circ\text{C}$  and  $\text{Soc}=50\%$

Using all the previous comments, a simplified model of a Lithium-ion cell can be represented by figure 10. A comparison of this model response with a VL7P battery response in figure 11 highlights the model accuracy. The errors is always less than 0.4 % for a current varying from -100A to 100A.

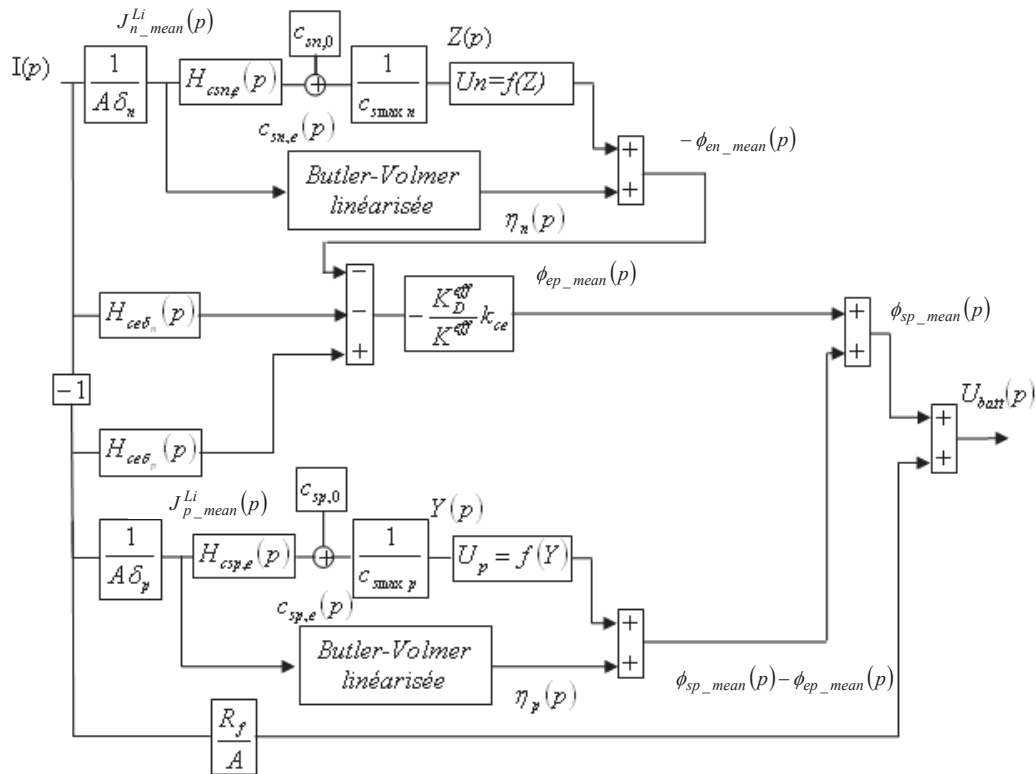


Figure 10 : Simplified model obtained

#### IV. CONCLUSION AND FUTURE WORK

In this paper a model for lithium-ion batteries has been proposed. This is a fractional model that stems from simplifications of an electrochemical model and is the result of this model partial differential equations solution (solution of diffusion equation (2)). Such an approach permits to get a simple model (low number of parameters in comparison with an approach based on Pade approximation that lead to an integer model with a large number of parameters) in which electrochemical variables and parameters still appear (parameters physical meaning is often with an approach based on model reduction). The obtained model permits to simulate the battery voltage with a relative error less than 0.5 %. This relative error value has been obtained through several validation tests (Merveillaut, 2011) (not presented here due to the limited number of pages) under various condition (state of charge, temperature, current values and sign). In future papers, the authors will present more simple models, obtained using additional simplifying assumptions and will show how these models has been used to estimate state of charge and available power.

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