Identification of electrochemical double layer capacitors using fractional models

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Abstract. The growing demand for storage systems of electric energy has made being developed a lot of devices. Among these devices, in recent years the supercapacitors have been increasingly boomed and more particularly the electrochemical double layer capacitors (EDLC). These devices, despite having a lower energy density than batteries, have a much higher power density. Consequently, there are a lot of mixed developments in which appear both devices together. For integrating EDLCs in storage systems, it is necessary to have a mathematical model which fits effectively. Obtaining a model is not trivial, because in operation involving diffusion phenomena of ionic liquids through porous electrodes it is not easily modeled. This fact makes the modeling of these devices be a line of very active research. Among the most commonly used models, it is possible to classify the next: based on RC networks with constant and variable capacitances with voltage, using distributed parameters and making use of fractional calculus among others. This article describes three models based on the topology of a resistor and a fractional capacitor in series. The influence of the resistance and the fractional non-integer order is analyzed, both for the charging and for the self-discharge stage. The study was conducted using capacitors with the next nominal capacitances $1F$, $10F$ and $100F$.

Key words

Electrochemical double layer capacitor, Fractional models, Electrical energy storing, Supercapacitor

1. Introduction

In recent years, demand for new systems for storing electrical energy, has increased a significant development of ultracapacitors, also known as electrochemical double layer capacitors, EDLC. EDLCs are elements capable of storing electrical energy electrostatically, without chemical reactions in the electrodes, having a very fast response and a high number of charge and discharge cycles without suffering damage. The characteristics of the EDLCs are complementary with current battery systems, so can be achieved mixed configurations (supercapacitors and batteries) that allow suit any system for storing and retrieving electric power .

In order to integrate EDLCs is necessary to model their behavior, turning out to be very different from traditional capacitors [1]. Several authors have proposed models based on the internal structure of the supercapacitor, considering the porous electrodes, the ionic liquids used, diffusion phenomena [2]. Others model the observed phenomena with several RC networks, or with a capacitance which is dependent of voltage [3, 4], and others have modeled these devices using fractional calculus [5, 6, 7]. All models attempt to represent the dynamic behavior, for simulating or for controling the dynamics of supercapacitors. In several fields of physics, there are numerous models using a fractional differential equation. This is very common, when there are conditions of fractal geometry and systems with distributed parameters [8, 9]. In electrical science, the current which goes through a capacitor is proportional to the non integer derivate of the voltage if at least one of the capacitor armature is rough [10, 11]. A network composed with infinite RC elements can be modeled by fractional differential equations [12, 13].

This paper presents a simple model for the dynamic behavior of supercapacitors. This model is based on the fractional calculus. With this model, satisfactory results are achieved. In turn, it is presented an improvement over the simple model, which shows high precision.

2. Dynamical models of EDLCs

The research in order to achieve electric models for supercapacitors has experienced considerable interest, and has many contributions in recent years. There are not fully satisfactory models, that provide insight and simulate the behavior thereof. Most current models use heuristic techniques to achieve improved structures and approaches. In most of them, a considerable number of variables is used, either a large number of passive elements or fractional variables models, and all are adapted to a time range of charge-discharge depending on the operating frequency. On supercapacitors electric model, it has been considered as a single entry system (current) and an output (voltage). The proposed model, is performed from the model of an ideal capacitor, and subsequently, it is added new elements to improve the resolution, which increases the model complexity.

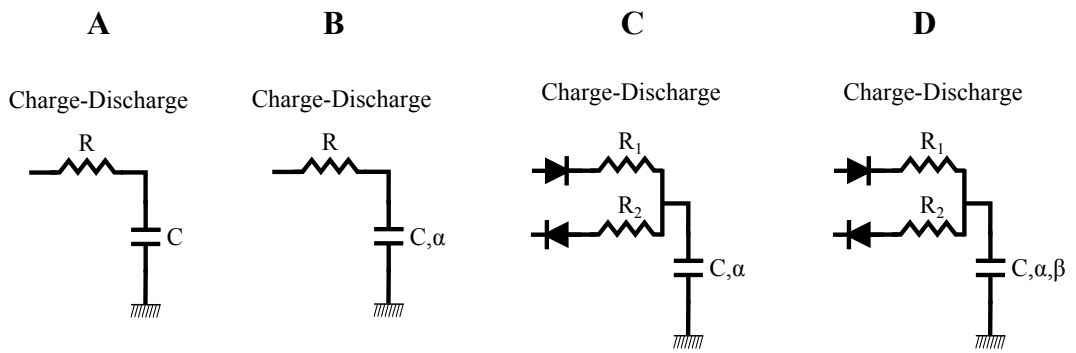

Figure 1: Analyzed and proposed models.

A. *Electric model*

The differential equation that relates the input current with the voltage across the terminals of a real capacitor is given by an ideal capacitor and a parasitic resistance (ESR). A set of models from a parasitic resistor in parallel with an ideal capacitor (EPR) it has been established, causing increased complexity in the models. In EDLCs, the values of the resistor in parallel with the capacitor are very high, so it has not been considered in this work, since its incorporation does not modify the results obtained here [11]. The resulting differential equation is:

$$v(t) = R \cdot i(t) + \frac{1}{C} \cdot \int i(t)\, dt \tag{1}$$

The transfer function or impedance in the Laplace domain is given as the ratio between the voltage and current .

$$\frac{V(s)}{I(s)} = G(s) = R + \frac{1}{C \cdot s} \tag{2}$$

This equation can be solved for simple input signals and there is no problem for complex signals using existing simulation programs. This circuit model it can be seen in fig. 1 (A model).

A first modification of the model (1) is by means of using differential equations models with non-integer order. The fractional relationship between voltage and current on the capacitor will cause a replacement of conventional derivative operator by a non-integer order derivative operator. The new transfer function is of the form:

$$\frac{V(s)}{I(s)} = G(s) = R + \frac{1}{C \cdot s^{\alpha}} \tag{3}$$

Where $G(s)$ is the relationship between the derivative of non-integer order of the voltage $V(s)$ with the current $I(s)$ that charge or discharge the supercapacitor [7]. This circuit model it can be seen in fig. 1 (B model).

1) EDLC model. Variation of the parasitic resistor ESR The model obtained in (3) has the same structure and passive elements with the same values in the charge and discharge of the EDLC. An improvement in this model is to maintain the same passive elements, resistance and fractional capacitor, but not their values. Thus, a first pattern is achieved by differentiating the charge resistor of the discharge resistor fig 1 C model. In this case, the model has a total of four parameters: R_1, R_2, C, and α corresponding to the charge and discharge resistors, capacitance and non-integer order, being :

$$\left| \begin{array}{l} i(t) \geq 0,\ charge,\ \ G_C(s) = R_1 + \frac{1}{C \cdot s^{\alpha}} \\ i(t) < 0,\ discharge,\ \ G_D(s) = R_2 + \frac{1}{C \cdot s^{\alpha}} \end{array} \right. \tag{4}$$

This model shows the existence of different values in the parasitic resistor (ESR), in the charge and discharge operation.

2) EDLC model. Variation of the parasitic resistor and the non-integer order A variation on the pattern obtained from (4) is to incorporate a variable non-integer order α, differentiating the charge operation of the discharge operation. In this case the number of parameters is increased considering the difference between of non-integer order of the charge operation α and the non-integer order of the discharge operation β. The proposed model is:

$$\left| \begin{array}{l} i(t) \geq 0,\ charge,\ \ G_C(s) = R_1 + \frac{1}{C \cdot s^{\alpha}} \\ i(t) < 0,\ discharge,\ \ G_D(s) = R_2 + \frac{1}{C \cdot s^{\beta}} \end{array} \right. \tag{5}$$

The models represented in (3)-(5) will be used in this work. In addition, experimental tests have been conducted to a set of EDLCs to display their behavior. The circuit model of this section it can be seen in fig. 1 (D model).

B. *Fractional differential equation solution*

The transfer function in each of the obtained models (equations (3), (4) or (5)), has two terms: the first one represents a proportionality with the input current and the second term corresponding to a fractional differential equation with constant coefficients . Without loss of generality , the output voltage of the supercapacitor is the sum of two values $v(t) = v_1(t) + v_2(t)$. The first term is proportional to the input current and the second term is obtained by solving fractional differential equation [14, 15]. The equation for the second term is of the form:

$$C \cdot D^{\alpha} v_2(t) = i(t) \tag{6}$$

The ratio of the Laplace transform of the output variable with respect to the input variable, called transfer function is:

$$\frac{V_2(s)}{I(s)} = G_2(s) = \frac{1}{C \cdot s^{\alpha}} \tag{7}$$

The inverse transform of this function equivalent to the response to the impulse function transfer $i(t) = \delta(t)$ is :

$$v2(t) = \frac{1}{C} \cdot \frac{t^{\alpha-1}}{\Gamma(\alpha)} \tag{8}$$

To solve the differential equation for any function $f(t)$, being zero the initial conditions , it is obtained:

$$v_2(t) = \frac{1}{C \cdot \Gamma(\alpha)} \int_0^t \frac{f(\tau)}{(t-\tau)^{1-\alpha}} d\tau = \frac{1}{C} \cdot D^{-\alpha} f(t) \tag{9}$$

being the solution to a function $f(t)$ continuous on the interval $[0, \infty]$. The values of the current signals used in this work are displaced step functions or displaced step function over time. Generalizing as an input signal , a unit step function displaced Δ seconds ($i(t) = u(t - \Delta)$, function $u(t)$ unit) , the equation (9) can be solved in this specific situation. Laplace transforms of the output voltage is :

$$V_2(s) = \frac{1}{C \cdot s^{\alpha+1}} e^{-\Delta s} \tag{10}$$

the solution of (10) is:

$$v_2(t - \Delta) = \frac{1}{C} \cdot \frac{(t-\Delta)^{\alpha}}{\Gamma(\alpha + 1)} \tag{11}$$

This equation will let obtain the time behaviour of the solution of the non-integer order differential equation, as long as the input signal be a decomposition of step functions with diferent displacements.

3. Materials and methods

To validate the proposed mathematical models, experimental data of the EDLCs are required, so there have been carried out a series of laboratory tests to obtain them. In this section, instrumentation and materials used are displayed, for this purpose. Besides the methodology for performing the tests.

A. *Materials*

In fig. 2 a basic diagram of the identification system used for laboratory testing is displayed. This equipment consists of the following elements :

1. A power operational amplifier **OPA549** *(Texas Instruments)*. This operational amplifier can provide a nominal current of $8A$, and also has a special input (i_{lim}) for limiting the output current of the amplifier. This is an important feature for implementing galvanostatic charge or discharge (by controlling the current) .
2. An analogical-digital convertion stage based on the precision converter **ADS1015** *(Texas Instruments)*. This stage has two differential analog inputs for measuring: the charging or discharging current and the voltage of EDLC. Current $i(t)$ is measured from the voltage of a resistor $R_m = 0.1\Omega$ which is arranged between the output of the operational amplifier and capacitor, and the EDLC voltage $v(t)$ directly. The circuit **ADS1015** has a $12Bit$ resolution, which sets a resolution of $3mV$ for the voltage measuring and $30mA$ for the current measuring.
3. Two digital-analogical convertion stage based on **MCP4725** (MICROCHIP) with a resolution of $12Bit$. These stages are used to control the charging-discharging processes of EDLC, for setting the voltage and current intensity references.
4. A microcontroller **ATmega328** model *(Atmel)*, implemented in the platform **Arduino Nano** *(Arduino)*. This microcontroller is responsible for directly controlling the galvanostatic charging process, so as to capture the data and send them to a PC for saving them.
5. A PC that is responsible for controlling and configuring the microcontroller for conducting the tests and storage of data, obtained from the measurements. This is achieved through a script made in javascript language under **Processing** *(Processing Foundation)*.

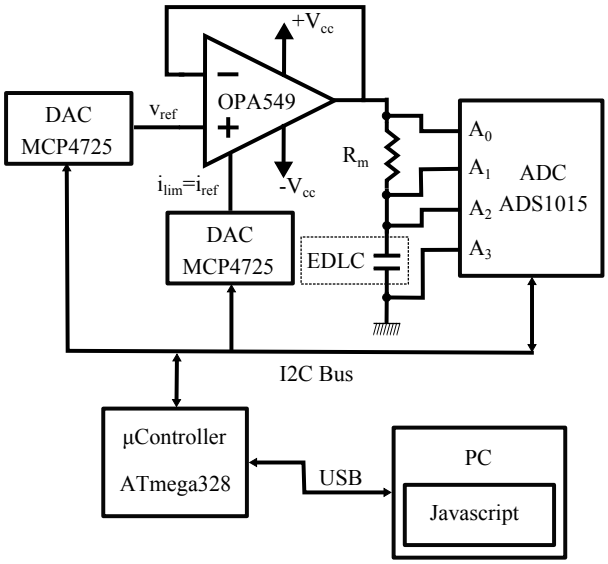

Figure 2: Basic diagram of the identification system.

B. *Methods*

Tests for data collection were performed using the following methodology : the EDLCs were shorted for at least 24 hours and then were charged by a current pulse, as can be seen in fig. 3 at the bottom. In the above figure, at top it can be seen that there are a set of three states in the charge test : a pre-condition to the load with a duration of $t_1 = 60s$, in which the EDLC is in open circuit voltage and its voltage is $v = 0$; another stage in which the constant galvanostatic charging current occurs to the rated maximum volt-

age, with t_2 duration established by the maximum voltage; and a third stage in which the EDLC is again at open circuit state in order to obtain data from self-discharge process for a fixed period of time $t_3 = 1h$.

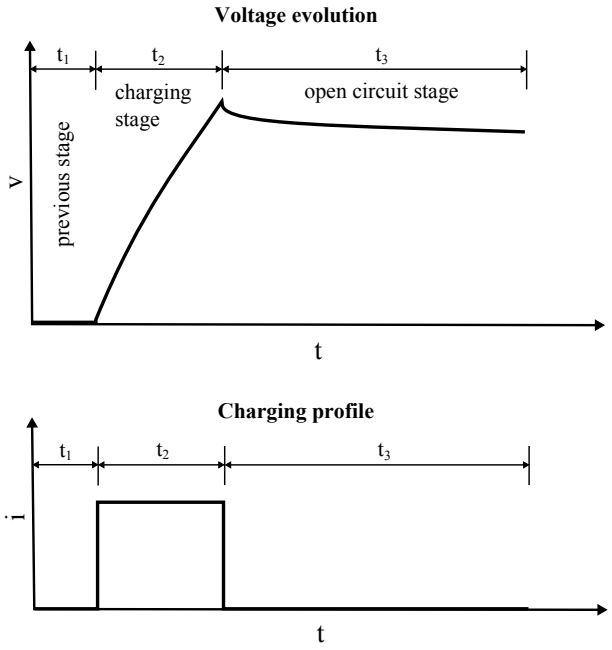

Figure 3: Galvanostatic charge method. Current profile $i(t)$ at bottom, voltage evolution $v(t)$ at top.

4. Identification and experimental data

Identification it has been performed by means of **Matlab**. This identification has been done from obtaining the transfer function parameters defined by (3), (4) and (5), which minimize a behaviour index. Next it is exposed the chosen index;

$$\sigma_D = \sqrt{\frac{\sum_{i=1}^{N} ((v)_{exp} - (v)_{cal})^2}{N-1}} \qquad (12)$$

where the subscripts represent the values obtained experimentally or calculated by model, and N is the number of points of the experiment. It has been used EDLCs of different capacitances and manufacturers. The selected capacitances have been 1, 10 and 100 farads, and two EDLC manufacturers: *PowerStor* ($1F$) and *Maxwell* ($10F$ and $100F$). In each of the following sections the results of identification are shown.

A. *Fractional model with constant parameters: charge-discharge*

It has been used a total of nine EDLCs: 3 of $1F$, 2 of $10F$ and 4 of $100F$. It has been done every fit, and it has been obtained the three parameters of this model. The fit results have been very good, which are displayed in Table 1. The results of the parameters clearly show the variability of resistor and capacitance values in all cases, being a factor that is repeated in all tests. There is no standard or trend in the devices tested. The capacitance specified by the manufacturer is not consistent with those obtained,

Table 1: Values of the model parameters defined by (3), B model.

Capacitance (F)	R	C	α	σ_D
1	0.237	1.103	0.96	0.007
1	0.378	1.101	0.949	0.007
1	0.228	0.705	0.939	0.016
10	0.486	8.76	0.943	0.01
10	0.446	9.367	0.941	0.009
100	0.418	84.561	0.965	0.022
100	0.388	86.825	0.967	0.021
100	0.49	83.455	0.957	0.027
100	0.453	86.371	0.96	0.025

generating discrepancies. Fractional non-integer order has high values, regardless of capacitance. The parasitic resistance (ESR) of this model proves to be variable, being smaller for capacitors with lower capacitance.

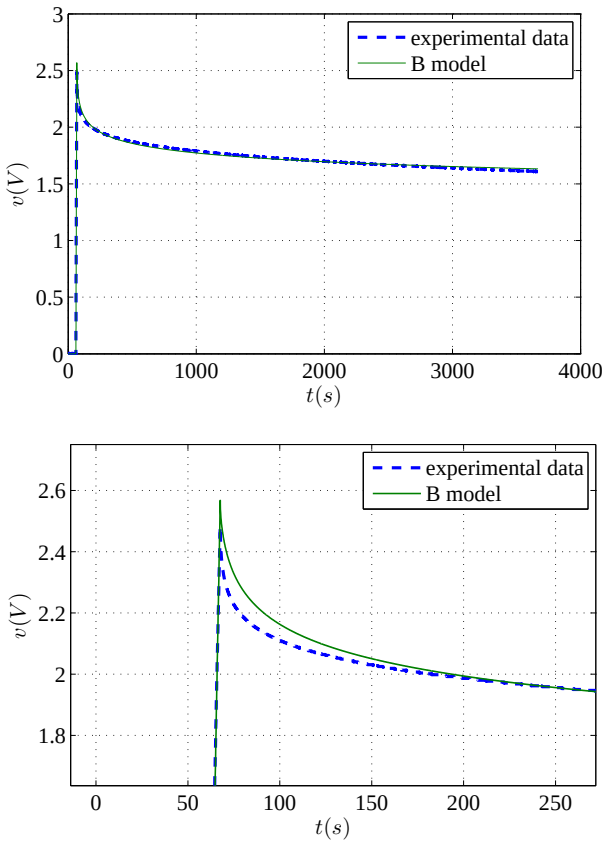

Figure 4: Experimental data and B model for a charge current of $i = 0.25A$ ($1F$ EDLC). Whole test at top, and zoomed detail at bottom.

B. *Fractional model with diferent resistor: charge-discharge*

In this section are displayed in Table 2 the fit made for the same supercapacitors using the model established in (4). There is a difference in the parasitic resistor (ESR), at charge and discharge operation, in all cases. It can not been generalize, if the resistors values are higher or lower in charging or discharging. As shown in the Table, for

lower capacity EDLCs, $1F$, the discharge resistor is higher than the resistor of the charge. The reverse effect is shown in higher power capacitors, $10F$ and $100F$. It can not be noticed big diferences among fits.

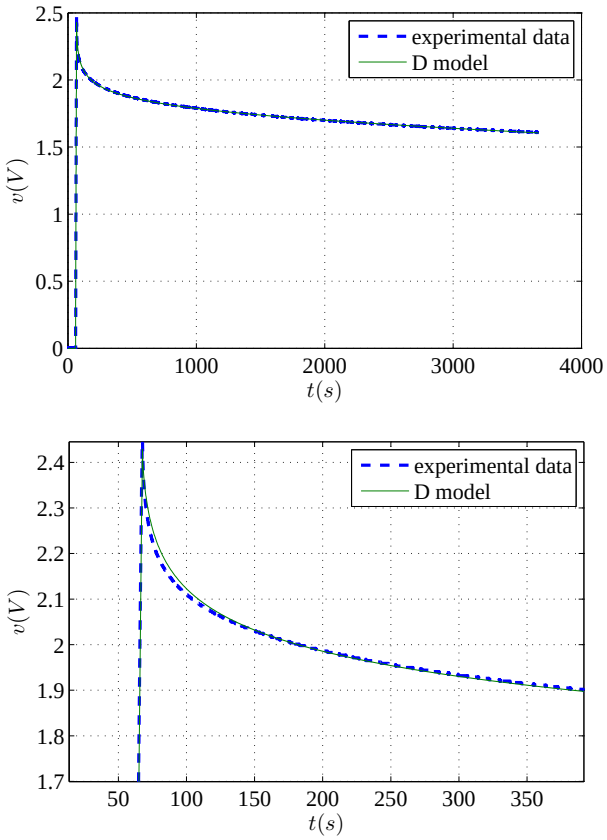

Figure 5: Experimental data and D model for a charge current of $i = 0.25A$ ($1F$ EDLC). Whole test at top, and zoomed detail at bottom.

C. *Fractional model with different value for resistors and for non-integer orders: charge-discharge*

The fits performed, with the model shown in equation (5), are shown in Table 3. Every fit has gotten a better fit than in the two previous cases, for (3) and (4) models. A very slight difference is observed between the rates of charge and discharge that indicates that this type of model does not provide any additional improvement obtained in the previous section.

In Figures 4, 5, 6, and 7 it is shown that the fit is improved at change in the input current, fitting very well with D model in the temporal response.

5. Conclusions

It has conducted a study of supercapacitors in order to obtain an electric model. There is a high mismatch in the parameters of the exposed models. There are no precise values beforehand in the capacitance or parasitic parameters (resistor or non-integer order) for any manufacturer or any capacitance value. The first proposed model was improved by incorporating elements that are depending on the sign of the current on the EDLC. It has introduced a

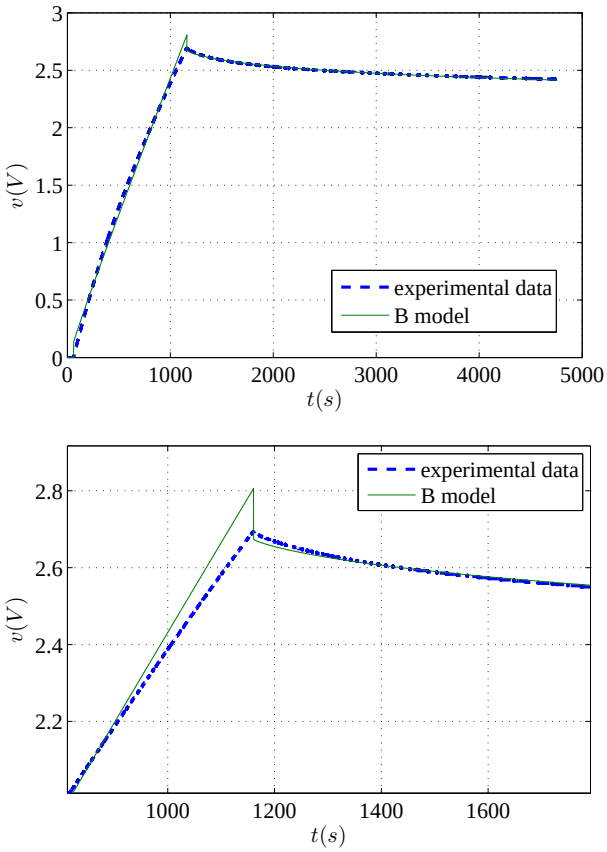

Figure 6: Experimental data and B model for a charge current of $i = 0.25A$ ($100F$ EDLC). Whole test at top, and zoomed detail at bottom.

simple way to simulate the elements with fractional derivatives when the input signal is a step or steps functions with delays. Two new circuits have been proposed to improve the model behavior compared to experimental results. It is improved, although the fit has increased the number of parameters and calculation for simulation.

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Table 2: Values of the model parameters defined by (4), C model.

Capacitance (F)	R_1	R_2	C	α	σ_D
1	0.092	0.105	1.1	0.96	0.008
1	0.056	0.624	1.041	0.953	0.008
1	0.176	0.119	0.708	0.938	0.016
10	0.525	0.439	8.803	0.943	0.01
10	0.47	0.417	9.399	0.941	0.009
100	0.468	0.336	84.48	0.963	0.022
100	0.431	0.317	86.76	0.965	0.021
100	0.541	0.404	83.244	0.955	0.027
100	0.498	0.379	86.202	0.958	0.025

Table 3: Values of the model parameters defined by (5), D model.

Capacitance (F)	R_1	R_2	C	α	β	σ_D
1	0.098	0.098	1.099	0.96	0.96	0.007
1	0.086	0.103	1.105	0.95	0.95	0.007
1	1.027	0.132	0.828	0.944	0.944	0.005
10	0.504	0.357	8.609	0.938	0.938	0.009
10	0.444	0.32	9.14	0.935	0.935	0.008
100	0.402	0.182	74.484	0.944	0.943	0.02
100	0.371	0.178	77.365	0.948	0.947	0.019
100	0.444	0.189	69.412	0.928	0.926	0.024
100	0.41	0.186	73.11	0.934	0.932	0.023

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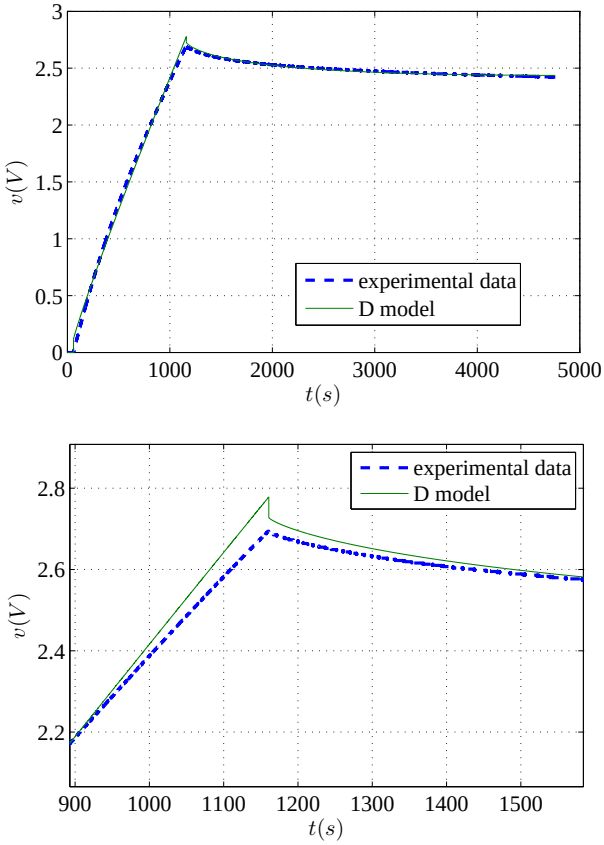

Figure 7: Experimental data and D model for a charge current of $i = 0.25A$ ($100F$ EDLC). Whole test at top, and zoomed detail at bottom.