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Identification of characteristic time constants in the initial dynamic response of electric double layer capacitors from high-frequency electrochemical impedance

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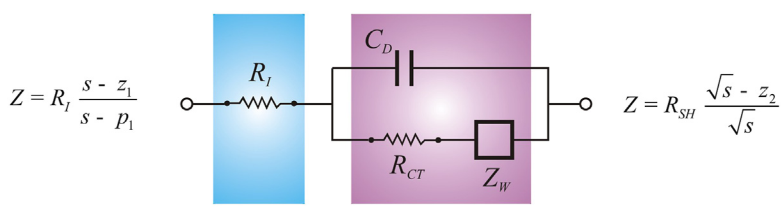
HIGHLIGHTS

- Zeros and poles of the high-frequency impedance of supercapacitors are analysed.
- Two different time constants describe the galvanostatic and potentiostatic controls.
- An analytical expression is derived for the time constant at the interfacial limit.
- PSpice program is used to do numerical inversion of the Laplace transform.

GRAPHICAL ABSTRACT



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ABSTRACT

The impedances of several electric double layer capacitors are analysed at high frequencies by using the Randles equivalent electric circuit with the semi-infinite Warburg impedance. The Warburg coefficient, the charge transfer resistance, the interfacial capacitance, as well as the geometric resistance of the devices are determined by means of a non-linear least squares fitting. Unlike other previous studies using this circuit, we identify the characteristic frequencies from the zero-pole representation at the limits of the Randles impedance at high and low frequencies. Our study includes the overlapping between the interfacial and porous transport processes in the equivalent series resistance at high frequencies and it additionally considers the frequency at the intersect point between the interfacial and porous regions in the impedance Nyquist plots. Evolution with time of the short-circuit current and the voltage drop in response to a current pulse in supercapacitors are theoretically analysed at the shortest times from numerical inversion of the Laplace transform by using PSpice®. The numerical results obtained from the Randles impedance and those from the low-frequency Warburg approximation are compared, and the significance of the different time constants is analysed and discussed.

1. Introduction

Electric double layer (EDL) capacitors [1] consist of two activated carbon porous electrodes separated by liquid electrolyte with a salt dissolved in an aqueous or organic solvent. They store electric charge and energy in the electric double layers at the electrolyte-electrode interfaces without the requirement of redox reactions and they are usually characterized, by analogy to conventional capacitors, by their capacitance, which is defined from the ratio of the stored electric charge to the electric potential drop across the electrodes. These devices show much higher specific energy than conventional capacitors due to high surface area of activated carbon porous electrodes [2]. They, together with batteries, store electric charges and renewable energy in a fast, safe and efficient manner so they find application in portable

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electronic devices and electric vehicles. Nowadays, there is a growing interest in EDL capacitors because, unlike batteries [3], they present high specific power, rapid charge-discharge capability, and long cycle life.

EDL capacitors exhibit problems such as self-discharging or open circuit voltage decay, capacitance losses at high frequencies and significant variations of capacitance and equivalent series resistance depending on the electric potential drop or the electric device used to discharge them [4–6]. Accordingly, electrochemical characterization of EDL capacitors is a classic research topic in the field of the electrochemical power sources. In recent years, different experimental techniques based on both potentiostatic and galvanostatic controls have been used to characterize this type of energy storage devices. These techniques include linear sweep voltammetry, cyclic voltammetry, galvanostatic charging-discharging, potentiostatic charging-discharging through a resistor or electrochemical impedance spectroscopy [7–20]. These studies focus on the determination of the capacitance at the longest times after the application of a constant or ramp perturbation using transient techniques or at the lowest frequencies using ac methods.

Electrochemical impedance spectroscopy [21] is a powerful method of characterising many of the electrical properties of a great variety of electrochemical systems and particularly power sources. Electrochemical impedance of porous electrodes systems based on the Randles equivalent electric circuit is a well-known topic since the work of Ho et al. [22]. The interfacial charge transfer processes occur at high frequencies and they usually appear in the Nyquist plot of the impedance as a semicircle in addition to a geometric resistance, while the transport process of the electrolyte inside the pores appears as Warburg-type impedances and it leads to a fully capacitive behaviour at the lowest frequencies [23]. Impedance functions usually find application in the small-signal dynamic modelling of supercapacitors, which has acquired special importance due to the increasing incorporation of these devices into sophisticated electric and electronic systems and the emerging convenience of interpreting the different parts of the whole system using similar procedures [24,25]. Although a number of studies have dealt with modelling of impedances of EDL capacitors by using electric circuits, including transmission lines and frequency dependent lumped elements, the high frequency regime has been much less considered than that at the lowest frequencies, especially when the interfacial process and the ionic transport process inside the pores are separated in a wide range of frequencies. Interpretation of the transient response of EDL capacitors at the shortest times after the application of external electric perturbations are generally based on the interpretation of impedance Nyquist plots and they have been usually done by using the time constant associated to the charging process of the interfacial capacitor through the charge transfer resistance [26]. However, this time constant corresponds to the characteristic frequency of a pole of the impedance function at the limit of high frequencies and, therefore, it is only appropriate when dealing with transient responses to current-controlled perturbations, i.e., under galvanostatic control [27,28]. When the supercapacitor is perturbed with a voltage-controlled signal under potentiostatic control, the characteristic frequencies correspond to the poles of the admittance function but interpretation of transient responses by using the related time constants has been poorly considered in literature. Also, the characteristic frequency and resistance at the intersect point between the interfacial and porous regions in the impedance Nyquist plots has been identified in supercapacitors [29,30]. However, no previous studies have been reported about the behaviour of the related time constant in the small-signal dynamic response of EDL capacitors.

The aim of this work is to identify the characteristic frequencies and time constants in the zero-pole representation of the limits of the high-frequency electrochemical impedance of EDL capacitors in order to get a better interpretation of the transient response of these devices at the shortest times after the application of current or voltage external perturbations. The experimental results for the electrochemical impedance of commercial capacitors are interpreted by considering the usual Randles equivalent electric circuit with the semi-infinite Warburg impedance. The Warburg coefficient, the charge transfer resistance, the interfacial capacitance, as well as the geometric resistance of each EDL capacitor have been determined by means of a non-linear least squares fitting. Unlike other previous studies using the Randles circuit [27,28,31] and others modelling general impedance functions by relaxation times distributions [32–39], we identify the characteristic frequencies from the zero-pole representation at the limits of the Randles impedance at high and low frequencies. Also, the equivalent series resistance at high frequencies takes into account the overlapping between the interfacial and porous transport processes. Moreover, our study additionally considers the frequency at the intersect point between the interfacial and porous regions in the impedance Nyquist plots. Evolution with time of the short-circuit current and the voltage drop in response to a current step in EDL capacitors are theoretically analysed at the shortest times from numerical inversion of the Laplace transform by the simulation of the small-signal equivalent electric circuit in the general purpose electric circuit simulation program PSpice®. The numerical results obtained from the impedance of the Randles equivalent electric circuit and those from the low-frequency Warburg approximation have been compared. Moreover, they have been compared to exponentials and Cottrell-type responses, which have been exactly or approximately derived from the limits of the high-frequency impedance of EDL capacitors. The significance of the interfacial time constants and that associated to the intersection point of the interfacial and porous regions in the impedance Nyquist plot have been analysed and discussed.

2. Experimental section

Four commercial EDL capacitors from Cooper Bussmann® have been investigated. They were used as received from suppliers. Characteristics of the EDL capacitors related to the equivalent serial resistance at 1 kHz, R_{SS}, the nominal capacitance, C_{nom}, and the rated voltage, V_m, specified by the manufacturer are listed in Table 1.

Impedance measurements were performed using the Agilent E498A precision LCR-meter in the range from 20 Hz to 2 MHz with the level at 10 mV amplitude at the open circuit potential, i.e., in a fully discharged state. Real and imaginary parts of impedance are gathered for each value of frequency with ten points per decade.

The open circuit voltage decay for the EDL capacitors, after charging potentiostatically at 2.0 V for 10 s, has been studied by means of the discharging through a resistor of 10 MΩ resistance. In all the cases we have obtained that the open circuit voltage decay is smaller than 0.1 V during the thirty first minutes.

Nominal capacitance of EDL capacitors was roughly checked from the measurement of the time constant during the potentiostatic charging process of each capacitor through a resistor of resistance 20 Ω by supplying a 1.0 V constant voltage. The obtained values from a fitting of the experimental data to an exponential increase curve, by additionally using the pulse amplitude as parameter, are 18.16 s for C1, 18.94 s for C2, 9.67 s for C3, and 22.45 s for C4. In all cases, the values obtained are in good agreement with those estimated from the nominal values of the capacitances.

Table 1
Characteristics of the EDL capacitors supplied by the manufacturer.

	Reference	R_{SS} (mΩ)	C_{nom} (F)	V_{max} (V)
C1	B0810-2R5105-R	500	1	2.5
C2	HV0810-2R7105-R	200	1	2.7
C3	PHV-5R4V74-R	400	0.47	5.4
C4	PHB-5R0V155-R	330	1.5	5.0