Journal of Power Sources 400 (2018) 457–467

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Review article

Review of fractional-order electrical characterization of supercapacitors

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HIGHLIGHTS

- Time & frequency domain, fractional-order characterization of super-capacitors.
- Performance metrics of supercapacitors depend on frequency & (dis)charging waveforms.
- Fractional-order expressions for capacitance, power & energy stored in supercapacitors.

ARTICLE INFO

Keywords:
Supercapacitor
Fractional-order analysis
Electrical characterization
Constant-phase element
Impedance spectroscopy
Effective capacitance

ABSTRACT

The tests and calculation of the key performance metrics of supercapacitors including capacitance, power and energy stored are commonly reported by the academia and the industry based on formulæ valid only for ideal capacitors. This is inconsistent with the fact that supercapacitors exhibit electrical behaviors that are different from those of ideal capacitors whether they are looked at in the time domain or in the frequency domain. This results inevitably in errors in their characterization, design and system integration. Based on recent literature, this review article is an attempt to present and discuss the main differences between ideal capacitors and supercapacitors, and especially how the performance metrics of the latter depend on the operating frequency, the charging/discharging waveform type as well as their deviation from ideality. We present a set of calculation methods for supercapacitor metrics using fractional-order calculus when such devices are operated under the commonly used (i) sinusoidal excitation, (ii) step current input and (iii) linear voltage input. We hope to bring such analysis, which is proven to be much more reliable and effective than the standard integer-order-based analysis of ideal capacitors, to the attention of researchers, manufacturers, and end-users of these devices particularly as their range of application is surging.

1. Introduction

Supercapacitors are electrochemical capacitors composed of two high surface area porous electrodes soaked in an ionic electrolyte and separated by a porous structure which prevents electrical short-circuit while permitting the movement of ions [1–6]. Unlike batteries and fuel cells that harvest the energy stored in chemical bonds through faradic reactions at the anode and cathode, it is commonly accepted that the properties of supercapacitors are principally the result of three different charge storage mechanisms that can coexist and contribute with varying proportions in the same device [1,6–9]. One mechanism is based on the nanometer-sized electrostatic charge separation at the interface between large surface area porous electrode material and the electrolyte (electric double layer), a second mechanism is attributed to highly reversible surface redox reaction during which partial faradic charge transfer occurs at the interface between the pseudocapacitive electrode material and the electrolyte, and a third one is due to diffusion-controlled ions intercalation, also in pseudocapacitive materials. In

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https://doi.org/10.1016/j.jpowsour.2018.08.047
Received 28 May 2018; Received in revised form 5 August 2018; Accepted 13 August 2018

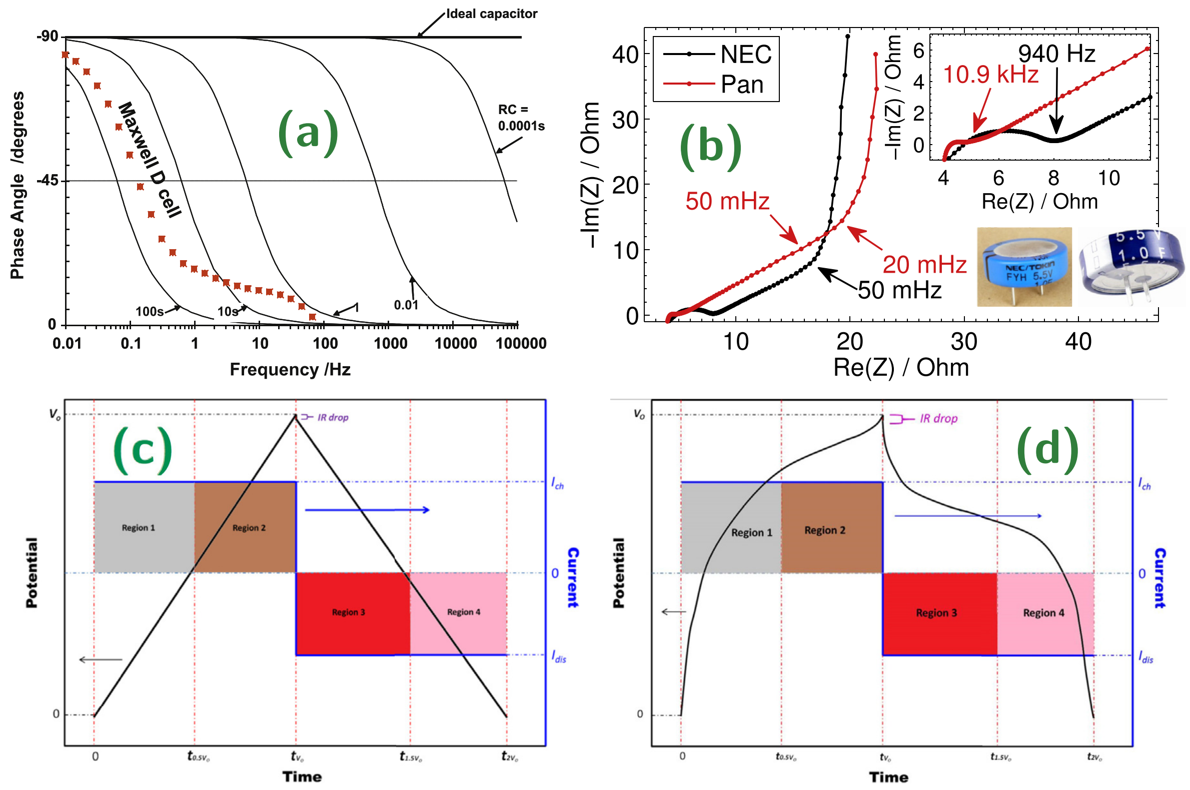

Fig. 1. (a) Impedance phase angle vs. frequency of a commercial electric double-layer capacitor (Maxwell Technologies D cell 350 F, part #BCAP0350E270T11) in addition to phase angles derived for several series-*RC* circuits, reproduced with permission [15]. (b) Nyquist impedance plot for two commercial supercapacitors (NEC/TOKIN 1 F part #FGR0H105ZF (denoted NEC) and Panasonic GC 1 F part #EECF5R5H105 (denoted PAN)), reproduced with permission [16]. Illustration of constant-current charge/discharge test result for (c) an electric double-layer capacitor (linear voltage-time profile), and (d) a pseudocapacitor (nonlinear voltage-time profile), reproduced with permission [17].

general, a voltage-independent current in response to a linear voltage scan, and a linear voltage-time profile in response to a constant-current charge/discharge of a supercapacitor assert that the device is rather an electrical double-layer capacitor [10]. While a deviation from these responses is an indication that the device exhibits a pseudocapacitance (see Fig. 1 (c)-(d)) [11–14].

Compared to rechargeable batteries, supercapacitors demonstrate outstanding power performance (as high as 10 kW kg^{-1}), a higher degree of reversibility and long cyclic life (>10^6 cycles), while remaining low-cost, maintenance-free and environmentally-compatible devices that can be easily integrated into electronic circuits and power systems [18]. Accordingly, supercapacitors are widely used as energy storage devices in a variety of applications where there is a high power demand, including solar energy harvesting systems for autonomous field devices [19], renewable power systems [20–26], hybrid energy storage systems [22,27–32], electric vehicles [31–38], uninterruptible power supplies [39,40], power regulators [41,42], ac line filtering [43–46], powering wireless sensor nodes [18,47] and biomedical implants [48], as well as other non-conventional applications [49–52]. Consequently, and given the different charge storage mechanisms mentioned above which may lead to nonlinear behavior, the proper characterization of supercapacitors performance metrics is crucial to their successful use in any given application in order to properly design other components of the system in terms of current rating and life time [53]. It is also important from a safety point of view.

Usually the assessment of the performance of supercapacitor devices is carried out through the three metrics: capacitance, equivalent series resistance and operating voltage, from which the power and energy stored can be computed [17]. Nonetheless, despite the clear difference between ideal capacitors and supercapacitors, the latter are still rated using a constant dc capacitance which assumes the same behavior as traditional capacitors. The time and frequency domain characteristics of supercapacitors are more complex than those predicted using the relationships of an ideal capacitor, i.e. $i_c(t) = Cdv_c(t)/dt$ (where $i_c(t)$ is the current in the capacitor resulting from a rate of change of an applied voltage $v_c(t)$ and $C = dq/dv_c$ is the capacitance measured in Farads) which translates into an impedance $Z_c = 1/sC$ ($s = j\omega$ is the Laplace transform operator). This difference can be demonstrated through the results reprinted in Fig. 1. In Fig. 1(a), the impedance phase angle vs. frequency response of a commercial double layer capacitor (Maxwell Technologies D cell 350 F, part #BCAP0350E270T11) and that of an ideal capacitor are shown. The close to -90° phase shift between the applied ac voltage and the measured ac current of Maxwell's D cell is restricted to a very limited frequency bandwidth close to dc. Beyond that, the device's behavior tends quickly toward that of a resistor. Meanwhile, the -90° impedance phase angle of the ideal capacitor extends over several decades. Thus, the frequency response of a supercapacitor cannot be modeled in a similar way to conventional capacitors using the basic electric elements. Fig. 1(b) shows the Nyquist plot of the real vs. imaginary impedance of two other commercial supercapacitors, namely NEC/TOKIN part #FGR0H105ZF and Panasonic GC part #EECF5R5H105, both rated 5.5 V, 1 F. It is clear that (i) the near-ideal behavior of both devices is not maintained if the operational frequency exceeds that of the knee frequency (different for both devices) although the two have the same rating, and (ii) for frequencies beyond a few tens of mHz, the devices operate in the Warburg mode of