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Further Experimental Evidence of the Fractional-Order Energy Equation in Supercapacitors

Ahmed S. Elwakil[1], Anis Allagui[2], T. J. Freeborn[3] and B. J. Maundy[4]

***Abstract*—Due to the dispersive porous nature of its material, carbon-carbon supercapacitors have a current-voltage relationship which is modeled by a fractional-order differential equation of the form $i(t) = C_\alpha \frac{d^\alpha v(t)}{dt^\alpha}$ where $\alpha \leq 1$ is a dispersion coefficient and C_α is a pseudo-capacitance not measurable in Farads. Hence, the energy stored in a capacitor, known to equal $CV^2/2$ where C is the capacitance in Farad and V is the voltage applied, does not apply to a supercapacitor. In a recent work [1], a fractional-order energy equation that enables the quantification of the energy stored in a supercapacitor when it is charged by a linear voltage ramp was derived. In addition, an effective capacitance (in proper Farad units) obtained from the time-domain analysis of the supercapacitor model under this type of charging was also derived. While some experimental results were given in [1], here we provide more experimental evidence of the applicability of the fractional-order energy equation using two commercial devices from two different vendors. We also show the effect of fast charging versus slow charging on the amount of energy stored in these supercapacitors.**

***Index Terms*—Supercapacitors, Fractional circuits, Impedance Spectroscopy, Constant Phase Element, Effective Capacitance.**

I. Introduction

Conventional electrostatic and electrolytic capacitors are widely used to hold micro- to pico-farad DC electric charge or to smooth out the leftover AC ripples on DC voltage busses. However, with the rapid developments in nanostructured materials and the growth of portable electronics and alternative energy sources, the demand for advanced high performance energy storage devices is soaring. Along with lithium ion batteries, supercapacitors are at the forefront of research and development in the energy storage field [2]. In contrast with Faradic reactions for chemical to electrical energy conversion in batteries, the electric performance of supercapacitors (also know as Electrical Double Layer Capacitors, EDLCs) are the results of charges being stored physically through adsorption/desorption of ions in the electric double-layer at the electrode material-electrolyte interface, and/or pseudo-capacitively through surface-confined reversible redox reactions [3]. Thus, theoretically tens of thousands of charge and discharge cycles are possible, with higher power density than batteries, and higher energy density than conventional capacitors [4].

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Due to the complex dispersive nature of new materials used in manufacturing supercapacitors, fractional-order models have been used to reduce the number of elements required to describe the frequency-dependent losses in these devices as well as to provide better fit to the experimental data [5]. A simple fractional-order circuit used to describe a supercapacitor is shown in the inset in Fig. 1 composed of an internal resistor R_s and a fractional-order capacitor (also known as the Constant Phase Element (CPE)) [6], [7], although other models have also been proposed in the literature [8]. This model has been successfully used to describe both frequency and time-domain behaviors of commercial supercapacitors [9], [10] where the impedance of an ideal capacitor $1/j\omega C$ is replaced with $1/(j\omega)^\alpha C_\alpha$, in which the pseudo-capacitance C_α is in units of F sec$^{\alpha-1}$ and α is the dispersion coefficient [11]. Note that $(j\omega)^\alpha = s^\alpha = \omega^\alpha \left(\cos\left(\frac{\alpha\pi}{2}\right) + j\sin\left(\frac{\alpha\pi}{2}\right)\right)$ with a phase angle $-\alpha\pi/2$.

Energy and power metrics of supercapacitors are crucial for the development of this energy storage technology [12]–[15] and its applications [16]–[19]. These metrics are determined by the electrode capacitance which is in principle surface-dependent. Surface heterogeneities and geometry-related distribution of current and potential at the electrode material, and the difference in size of solvated ions vs. volume of pores make the capacitance frequency-dependent. This is experimentally observed as the far-from-vertical complex impedance plot in Nyquist form shown in Fig. 1 for a demonstrative commercial supercapacitor rated by the manufacturer as a 1 Farad device (NEC/TOKIN, unit# FGR0H105ZF) with a maximum operating voltage of 5.5V. In the same figure, the fitting of the measured impedance to the $R_s - CPE$ model ($Z = R_s + 1/(j\omega)^\alpha C_\alpha$) (dotted straight lines) is shown to provide acceptable accuracy. Noting that supercapacitors are mainly used as energy backup devices, it is clear that the lower end of the frequency range (close to DC) is more important for estimating the energy storing capability of the device [17]. From Fig. 1, it is seen that in the frequency range 50mHz-10mHz the model parameters are $(R_s, C_\alpha, \alpha) = (14.4, 0.436, 0.842)$ with units as indicated. Therefore, applying the energy equation $E = CV^2/2$ to estimate the energy stored in this device would definitely lead to a significant over estimation since the manufacturer rated capacitance of 1 Farad is given at DC, whereas even at a few mHz frequency, the device has already lost a significant portion of its capacitive behavior. This over estimation will drastically increase if a wider operating frequency range is considered; for example if supercapacitors are employed in 50Hz or 60Hz power line applications.