Extended $RC$ Impedance and Relaxation Models for Dissipative Electrochemical Capacitors

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Abstract— Electrochemical capacitors are a class of energy devices in which complex mechanisms of accumulation and dissipation of electric energy take place when connected to a charging or discharging power system. Reliably modeling their frequency-domain and time-domain behaviors is crucial for their proper design and integration in engineering applications, knowing that electrochemical capacitors in general exhibit anomalous tendency that cannot be adequately captured with the traditional $RC$-based models. In this study, we first review some of the widely used fractional-order models for the description of impedance and relaxation functions of dissipative resistive–capacitive system, namely, the Cole–Cole, Davidson–Cole, and Havriliak–Negami models. We then propose and derive new $q$-deformed models based on modified evolution equations for the charge or voltage when the device is discharged into a parallel resistive load. We verify our results on anomalous spectral impedance response and time-domain relaxation data for voltage and charge obtained from a commercial supercapacitor.

Index Terms— Fractional-order calculus, $H$-function, impedance spectroscopy, $q$-exponential, relaxation response, supercapacitors.

I. INTRODUCTION

Electrochemical capacitors are energy storage devices relying on the very large electric double-layer capacitance at the porous electrode/electrolyte interface for electrostatic charge storage and/or fast and reversible faradic redox reactions for pseudocapacitive storage [1], [2]. Their capacitance, potential window, energy, and power capabilities are dependent on several geometrical and physical parameters, including the surface area, type and microstructural complexity of the electrodes being used, interfacial charge absorption/transfer, ions’ electrodifussion and migration dynamics, types of supporting electrolyte and ionic strength, etc. [3]. The direct identification of their physical parameters and characterization of underlying microscopic processes occurring in such systems is quite challenging. It often requires sophisticated systems of instrumentation with high in situ accuracy and resolution levels. However, this can be circumvented to a certain extent by analyzing instead the measurements of macroscopic quantities (current and voltage) in time-domain relaxation experiments or from frequency-domain impedance or admittance [4], [5]. Such information allows one to gain useful insight into the microscopic processes taking place in the system without going into unnecessary details. Furthermore, it is important for practical purposes to be able to describe a system in the frequency domain when time-domain data are available, and vice versa, describing the system in the time domain when the data available are in the frequency domain using appropriate transformations [6], [7], [8]. Of course, it is understood that frequency-domain formulation becomes inappropriate when the system under consideration involves nonlinear, local-in-time effects. This makes time-domain formulation more convenient in this context.

The simplest type of electrochemical capacitors, i.e., electric double-layer capacitors (EDLCs), can be viewed as an idealy nonpolarizable two-electrode cell system, where faradaic reactions occur very fast and the charge transfer resistance is negligible. They can be modeled using a parallel $RC$ circuit representing the bulk resistance and bulk capacitance of the device, which is usually a good starting point to model their behavior [3]. We assume the series resistance to be negligible for modeling convenience. The relaxation response of an $RC$ circuit is a decaying exponential function with time (with a single characteristic relaxation constant $\tau$), which is known to be the eigenfunction of the first-order time derivative operator, i.e., the evolution equation $d\rho(t)/dt + \tau^{-1}\rho(t) = 0$ [see (3) below]. However, it is becoming evident from many experimental data that the relaxations of porous electrodes and complex electrochemical capacitors in general are rather
nonexponential, power-law-like profiles [5]. From frequency-domain measurements, the corresponding impedance does not show the expected semicircle of imaginary versus real parts of an ideal RC circuit [9]. These observations indicate that from a macroscopic point of view the system cannot be viewed simply as the collection of many ideal, noninteracting subsystems.

Anomalies in the electrical response and frequency dispersion of materials and devices in general are the characteristic features of disorder, spatial heterogeneity (e.g., fractal and porous structures), and wide spectrum of relaxation times. The treatment of such type of data usually requires extending the traditional kinetic equation \( d\rho(t)/dt + \tau^{-1}\rho(t) = 0 \) using tools borrowed from fractional calculus. This leads to the well-known fractional impedance models of Cole–Cole [10], Davidson–Cole [11], and Havriliak–Negami [12] which can be viewed as extension of the Debye model by introducing one or two fractional exponents [13], [14], [15]. Their corresponding time-domain relaxation dynamics are expressed in terms of the Mittag–Leffler (ML) and Fox’s H-functions [13]. In this study, after reviewing the above-mentioned fractional models, we propose and derive new deformed dynamic models for porous structures, and wide spectrum of relaxation times. The characteristic relaxation functions of materials and devices in general are the characteristic of the Cole–Cole–Davidson–Cole, and Havriliak–Negami type. Subsequently, the \( q \)-deformed models are derived and discussed in Section IV.

The frequency-domain and time-domain experimental results measured on a commercial supercapacitor are analyzed and modeled in Section V.

II. CLASSICAL RC MODEL

First, we recall that the impedance of a parallel RC circuit model is given by the ratio of the Laplace transforms [defined as \( \mathcal{L}(f(t); s) = F(s) = \int_0^\infty f(t)e^{-st}dt \)] of time-domain voltage \( v(t) \) and current \( i(t) \) as

\[
Z(s) = \frac{\mathcal{L}(v(t))}{\mathcal{L}(i(t))} = \frac{V(s)}{I(s)} = \frac{R}{1 + \frac{s}{\tau}}
\]

where \( s = j\omega \) and \( \tau = RC \) is a characteristic relaxation time. Equation (1) has the same form as the normalized complex susceptibility model of dielectrics provided by Debye, i.e., \( \chi(t) = \frac{1}{1 + \frac{t}{\tau_D}} \). Its corresponding response function obtained by inverse Laplace transform of \( \chi(t) = \phi(t) = \mathcal{L}^{-1}(\chi(s); s) = \tau_D^{-1}e^{-t/\tau_D} \) \((t > 0)\). The relaxation function defined as \( \Psi(t) = 1 - \mathcal{L}^{-1}(\chi(s); s; t) \) in this case is equal to \( e^{-t/\tau_D} \) [16], with a half lifetime characteristic, representing the time at which \( \Psi(t) \) reaches half of its initial value, being \( \tau_D \ln(2) \approx 0.693 \tau_D \).

In the same way, the time-domain voltage decay of the capacitor, which we denote \( \rho(t) \), corresponding to its discharge into a parallel resistance from an initial charge \( \rho(0) = 1 \) is given by

\[
\rho(t) = e^{-t/\tau}.
\]

Equation (2) also represents the evolution of the electrical charge as the precharged capacitor self-discharges into the parallel resistance. It is also the solution of the linear integer-order differential equation

\[
\frac{d\rho(t)}{dt} + \tau^{-1}\rho(t) = 0.
\]

This is the equation of the standard kinetic model in which the rate of charge \( d\rho(t)/dt \) of a certain physical quantity \( \rho(t) \) as it is approaching equilibrium by the action of an external excitation is proportional to the quantity itself. Generalizations of (3) using different forms of fractional-order, instead of integer-order, time derivatives of \( \rho(t) \) are presented in Section III. Models obtained when elevating \( \rho(t) \) to a power of \( q \) \((q \in \mathbb{R})\) while maintaining the integer-order derivative in (3) are presented and discussed in Section IV.

III. FRACTIONAL-ORDER MODELS

Generalization of the Debye models for complex susceptibility and relaxation function in dielectrics include the nonexponential Cole–Cole [10], Davidson–Cole [11], and Havriliak–Negami [12] models. Equivalently, the normalized Cole–Cole impedance model is given by [10]

\[
Z_\alpha(s) = \frac{1}{1 + (s\tau_\alpha)^\alpha} \quad (0 < \alpha \leq 1)
\]

which admits the time-domain voltage or charge relaxation in terms of the ML function as [5], [16]

\[
\rho_\alpha(t) = 1 - (t/\tau_\alpha)^\alpha E_\alpha,1^\alpha[-(t/\tau_\alpha)^\alpha] = E_\alpha,1^\alpha[-(t/\tau_\alpha)^\alpha]
\]

Fig. 1. Graphical comparison between (a) first-order, local derivative of a function \( f(t) \) versus (b) its fractional-order, nonlocal derivative that takes into account not just the immediate past of the function proceeding the instant \( t \) but also the whole past of the function.
where the initial condition is \( \rho_\theta(0) = 1 \). This result is obtained from Prabhakar integral [17], [18]

\[
\int_0^\infty t^{\beta-1} E_{\alpha,\beta}(-at^\alpha) e^{-mt} dt = \frac{s^{-\beta}}{(1 + a s^{-\alpha})^\gamma} = \frac{s^{\alpha - \beta}}{(s^\alpha + a)^\gamma}
\]

(7)

where

\[
E_{\alpha,\beta}(z) := \sum_{k=0}^{\infty} \frac{(\gamma)_k}{\Gamma(\alpha k + \beta)} z^k \quad (\alpha, \beta, \gamma \in \mathbb{C}, \text{Re}(\alpha) > 0)
\]

(8)

[with \((\gamma)_k = \gamma(\gamma + 1), \ldots, (\gamma + k - 1) = \Gamma(\gamma + k)/\Gamma(\gamma)\) being the Pochhammer symbol and \(\Gamma(z)\) is the gamma function] is the three-parameter ML function. At the limit of \( \alpha \to 1 \), one readily recovers the Debye function \( E_1(z) = e^{-z} \). The half lifetime characteristic can be obtained from the inverse of the ML function [19], [20]. We note that (6) can be expressed in terms of Fox’s \( H \)-function (see the Appendix) as [13]

\[
\rho_\theta(t) = H_{1,2}^1 \left[ \frac{(t/\tau_\alpha)^\alpha}{(0,1)(0,0,a)} \right].
\]

(9)

Equation (6) is also the solution to [21]

\[
\frac{d\rho_\theta(t)}{dt} + t^{-\alpha}D_t^{-\alpha}\rho_\theta(t) = 0
\]

(10)

with \( \rho_\theta(0) = 1 \), and \( D_t^{-\alpha}f(t) = (d/dt)_0 D_t^{-\alpha}f(t) \) denotes the fractional derivative in the Riemann–Liouville sense with

\[
\rho_\theta(t) = H_{1,2}^1 \left[ \frac{(t/\tau_\alpha)^\alpha}{(0,1)(0,0,a)} \right].
\]

(11)

being the Riemann–Liouville fractional integral. Equation (6) is also the solution to [16]

\[
C_0 D_t^{-\alpha}\rho_\theta(t) + t^{-1}\rho_\theta(t) = 0
\]

(12)

where \( C_0 D_t^{-\alpha}\) is defined here in the Caputo sense by [22]

\[
C_0 D_t^{-\alpha}f(t) = \frac{1}{\Gamma(1 - \alpha)} \int_0^t (t - \tau)^{-\alpha} \frac{df(\tau)}{dt} d\tau.
\]

(13)

Equation (10) or (12) is one way of generalizing the integer-order rate equation given by (3) by having global, nonlocal time derivative of \( \rho_\theta(t) \) proportional to the quantity itself, and thus including memory effects [21], [23], [24], [25], [26].

On the other hand, the (normalized) Davidson–Cole impedance model is given by [11]

\[
Z_\theta(s) = \frac{1}{(1 + s \upsilon)^\beta} \quad (0 < \beta \leq 1)
\]

(14)

and its corresponding relaxation function [with the use of (7)] is [13], [16]

\[
\rho_\theta(t) = \frac{\gamma(\beta, t/\tau_\beta)}{\Gamma(\beta)} = 1 - \frac{1}{\Gamma(\beta)} H_{1,2}^1 \left[ \frac{(t/\tau_\beta)^\alpha}{(\beta,1)(0,1)} \right]
\]

(16)

where \( \gamma(a, z) = \int_0^\infty x^{a-1}e^{-x} dx \) is the complementary incomplete gamma function. The corresponding differential equation for \( \rho_\theta(t) \) with the usual initial condition \( \rho_\theta(0) = 1 \) is in this case [21], [27]

\[
\frac{d\rho_\theta(t)}{dt} + t^{-\beta}D_t^{-\beta}\rho_\theta(t) = 0
\]

(17)

with the use of the Kilbas–Saigo–Saxena integral operator [28]

\[
\rho_\theta(0) = 1 - (t/\tau_\beta)^\alpha E_{\alpha,\beta}(\alpha,\beta,\tau_\beta) = 0
\]

(18)

Finally, the Havriliak–Negami impedance function is a further generalization of the Cole–Cole and Davidson–Cole models, and it is given by [12]

\[
Z_H(s) = \frac{1}{(1 + (s \upsilon)^\beta)^\beta} \quad (0 < \alpha, \beta \leq 1).
\]

(19)

For \( \beta = 1 \), we recover the Cole–Cole model, while for \( \alpha = 1 \), the Davidson–Cole model is recovered, and with \( \alpha = \beta = 1 \) we end up with the Debye model. From (7), the corresponding relaxation function for the Havriliak–Negami model can be expressed in terms of the ML function as [16]

\[
\rho_H(t) = 1 - (t/\tau_H)^\beta E_{\alpha,\beta}(\alpha,\beta,\tau_H) = 0
\]

(20)

or in terms of the \( H \)-function as [13], [16], [29]

\[
\rho_H(t) = 1 - \frac{1}{\Gamma(\beta)} H_{1,2}^1 \left[ \frac{(t/\tau_H)^\alpha}{(\beta,1)(0,1)} \right] = 0.
\]

(21)

The differential equation for \( \rho_H(t) \) is [21], [27]

\[
\frac{d\rho_H(t)}{dt} + \sum_{k=0}^{\infty} \tau_H^{-\alpha(k+1)} D_t^{-\alpha(k+1)} \rho_H(t) = 0.
\]

(22)

Note that apart from the above time-domain relaxation functions, their frequency-domain counterparts can also be expressed in terms of the \( H \)-function (see Hilfer [30]).

IV. \( q \)-DEFORMED MODELS

Now if the first-order time derivative of \( \rho(t) \) in (3) is taken instead proportional to a power of \( \rho(t) \) such that

\[
\frac{d\rho_\theta(t)}{dt} + \frac{\rho_\theta(t)}{\tau_\theta} = 0
\]

(23)

where \( q_1 \) is a real parameter, then the solution for \( \rho_\theta(t) \) with \( \rho_\theta(0) = 1 \) admits the power-law behavior

\[
\rho_\theta(t) = \left[ 1 - (1 - q_1 t/\tau_\theta) \right]^{-q_1} = e_{q_1}^{-t/\tau_\theta}
\]

(24)

where \( e_q^x \) is defined as the \( q \)-exponential function [31]. We note here some of its properties: 1) for \( q < 1, e_q^x = 0 \) for \( x < -1/(1-q) \) and \( e_q^x = 1 + (1-q)x^{1/(1-q)} \) for \( x \geq -1/(1-q) \); 2) for \( q = 1, e_q^x = e^x \) for \( \forall x \); and 3) for \( q > 1, e_q^x = 1 + (1-q)x^{1/(1-q)} \) for \( x < 1/(q-1) \) [31]. Its Taylor series expansion is

\[
e_{q}^{-x} = e^{-x} \left[ 1 + \frac{1}{2} q (q - 1) x^2 - \frac{1}{3} (q - 1)^2 x^3 + \cdots \right]
\]

(25)
from which it is clear that at the limit $q \to 1$, one recovers the ordinary exponential law $\rho(t) = e^{-t}$ [i.e., (2)].

We note also that the $q$-exponential and $q$-Gaussian distributions are the functions associated with some systems showing quasi-stationary states and are the maximizing distributions for the nonadditive Tsallis entropy [32]

$$S_q = -k \sum_i p_i^q \ln_q(p_i)$$  \hspace{1cm} (26)

where $k$ is a positive constant, $q \neq 1$, and $p_i = p(E_i)$ is the probability that the system is in the $i$th configuration and satisfying $\sum_i p_i = 1$. The function

$$\ln_q(x) = \frac{x^{(1-q)} - 1}{1 - q} \hspace{1cm} (x > 0)$$  \hspace{1cm} (27)

denotes the $q$-logarithm, inverse of the $q$-exponential, i.e., $\ln_q[\exp_q(x)] = \exp_q[\ln_q(x)] = x$ [33]. It is clear that as $q \to 1$, $\ln_q(x) \to \ln(x)$, and one recovers the Boltzmann–Gibbs entropy $S_1 = -k \sum_i p_i \ln(p_i)$ ($k = k_B$ is the Boltzmann’s constant) associated with the standard exponential and the Gaussian distribution [32].

The $q$-exponential function also arises from the Laplace transform of the Gamma probability density function (pdf) [34]. This means that an EDLC described by (23) and (24) can be viewed as a spatially distributed network of subsystems, each of which follows the tradition exponential RC decay ($e^{-t/\tau}$) with time constants following the Gamma pdf [34], [35]. The value of the parameter $q$ is related to the shape factor of the Gamma distribution [34].

Alternatively to the modified evolution equation given by (23), from the $q$-difference defined as [36]

$$x \Theta_q y = \frac{x - y}{1 + (1 - q)y} \hspace{1cm} (y \neq 1/(q - 1))$$  \hspace{1cm} (28)

and the $q$-derivative defined as [36]

$$D_q f(x) = \lim_{y \to x} \frac{f(x) - f(y)}{x \Theta_q y} = \left[1 + (1 - q)x\right] \frac{df(x)}{dx}$$  \hspace{1cm} (29)

with the corresponding $q$-integral

$$\int_0^x f(x) dx = \int \frac{f(x)}{1 + (1 - q)x} dx$$  \hspace{1cm} (30)

both under the condition that $[1 + (1 - q)x] \neq 0$, the result given in (24) can also be obtained from the solution of the deformed differential equation

$$D_{q(t)} \rho_{q(t)}(t) \equiv \left[1 - (1 - q(t))/\tau_{q(t)}\right] \frac{d\rho_{q(t)}(t)}{dt} = -\frac{\rho_{q(t)}(t)}{\tau_{q(t)}}$$  \hspace{1cm} (31)

Again at the limit of $q_1 \to 1$, one evidently retrieves $\rho(t) = e^{-t/\tau}$; otherwise, for $q_1 < 1$, (24) belongs to a particular case of a type-1 beta family of functions and for $q_1 > 1$ (by writing $1 - q_1 = -(q_1 - 1)$), (24) belongs to a particular case of a type-2 beta family of functions [37], [38], [39], [40], [41], [42]. The half lifetime characteristic in this case is

$$t_{1/2} = \frac{\tau_{q_1}}{2 \ln_q(2)}$$  \hspace{1cm} (32)

which tends to the usual decaying law $\tau \ln(2)$ as $q_1 \to 1$.

Finally, we note that from (24) with $Z_q(s) = s \mathcal{L}((1 - \rho_{q(t)}(t))/s) = 1 - s\mathcal{L}(\rho_{q(t)}(t); s)$ that the following impedance function is obtained:

$$Z_{q_1}(s) = 1 - \eta e^{s/2} (1 - k_1, \eta)$$  \hspace{1cm} (33)

where $k_1 = 1/(q_1 - 1)$ and $\eta = k_1 \tau_{q_1}$. On the other hand, the dual derivative operator in (29) is defined as [36]

$$D_{(q)} f(x) = \lim_{y \to x} \frac{f(x) \Theta_{q(x)} f(y)}{x - y} = \frac{1}{[1 + (1 - q)f(x)]} \frac{df(x)}{dx}$$  \hspace{1cm} (34)

with its corresponding $q$-integral

$$\int_0^x f(x) \Theta_{q(x)} dx = \int \frac{f(x)}{1 + (1 - q)x} f(x) dx$$  \hspace{1cm} (35)

with $[1 + (1 - q)f(x)] \neq 0$. Using such a definition, one obtains as a solution for the nonlinear ordinary differential equation

$$D_{(q)} \rho_{q_2}(t) \equiv \frac{1}{[1 + (1 - q_2)\rho_{q_2}(t)]} \frac{d\rho_{q_2}(t)}{dt} = -\frac{\rho_{q_2}(t)}{\tau_{q_2}}$$  \hspace{1cm} (36)

the following result in terms of the logistic function:

$$\rho_{q_2}(t) = \frac{1}{(q_2 - 1) + (2 - q_2)e^{q_2 t}}$$  \hspace{1cm} (37)

It is evident that at the limit $q_2 \to 1$, one retrieves the traditional exponential decay given by (2). The half lifetime is

$$t_{1/2} = \tau_{q_2} \ln \left(\frac{3 - 2q_2}{2 - q_2}\right)$$  \hspace{1cm} (38)

which reduces as expected to $\tau_{D_2} \ln(2)$ as $q_2 \to 1$. The impedance function corresponding to (37) is

$$Z_{q_2}(s) = 1 + \frac{\tau_{q_2} s}{(q_2 - 1)(1 + \tau_{q_2} s)(1 - (\kappa_2)^{-1})}$$  \hspace{1cm} (39)

where $_2F_1(a, b, c, z)$ is the hypergeometric function and $\kappa_2 = 1/(q_2 - 1)$. It simplifies to $(1 + s \tau_{D_2})^{-1}$ at the limit of $q_2 = 1$.

V. EXPERIMENTAL RESULTS

The electrical measurements were carried out on a commercial Samson supercapacitor, part No. DRL105S0TF12RR, rated 2.7 V, 1 F using a Biologic VSP-300 electrochemical station equipped with impedance spectroscopy module. The spectral impedance results were obtained at open-circuit voltage with stepped sine excitations from 100-kHz to 10-mHz frequency and with 10-mV rms amplitude. The time-domain charge and discharge measurements were conducted as follows. First, the device was precharged with constant current–constant voltage (CCCV) mode: 100 mA up to the nominal voltage of 2.7 V, and then the voltage was maintained at 2.7 V for 5 min. For the subsequent discharge step, the potentiostat acted as a constant resistor $R$ (2, 10, and 50 Ω) for the duration necessary for the voltage to drop from 2.7 V to 3 mV.
A. Impedance Spectroscopy

Plots of magnitude of impedance versus frequency are shown in Fig. 2(a). We limited the frequency range to [0.01; 1.41] Hz where the device is mostly capacitive [9]. Beyond this upper limit, \( RC \) or modified \( RC \)-based circuits are not suitable to analyze the data and other electrical elements may have to be considered. Superposed on the experimental data are fitting by the metaheuristic particle swarm optimization (PSO) technique [43] using the six models given by (1) (denoted "exp" in the legend), (4) ("CC"), (14) ("DC"), (19) ("HN"), (33) ("q-exp"), and (39) ("logistic"). The models' parameters are given in the figure caption. In Fig. 2(b) and (c), we show the corresponding errors in magnitude of impedance versus frequency and in box plot format, respectively. Fig. 2(d) depicts the experimental impedance phase angle versus frequency and fitting using the six models presented in this study. The same is shown in Fig. 2(e) for the real versus imaginary parts of impedance with the frequency being an implicit variable. The deviation from the \(-90^\circ\) phase angle in Fig. 2(d) and the nonvertical profiles in Fig. 2(e) indicate the nonideal capacitive-resistive behavior of the device. Detailed analysis of spectral impedance of EDLCs can be found for instance in [9].

It is clear from these results that fitting with the fractional-order models outperforms those done with the \( q \)-deformed models. The root mean square errors (RMSEs) over the frequency range [0.01; 1.41] Hz are 0.042, 0.005, 0.005, 0.038, and 0.037 for (1), (4), (14), (19), (33), and (39), respectively. Furthermore, an important advantage of the fractional-order impedance models is the simplicity of the expressions which makes their computation much more efficient than the newly proposed \( q \)-deformed models. The latter ones involve computational considerations with the numerical estimation of the incomplete gamma function [see (33)] or the infinite sum in the hypergeometric function [see (39)]. Nonetheless, the errors associated with the \( q \)-deformed models are still comparatively reasonable and slightly better than the classical \( RC \) model.

B. Discharge Response

The results for the first 60 s of the discharge relaxation sequence for the case of \( R = 2 \ \Omega \) are shown in Fig. 3(a) in terms of normalized voltage versus time and in Fig. 3(d) for the normalized charge versus time. The resistive load of \( R = 2 \ \Omega \) is taken as an illustrative example as the same conclusions can be drawn from the other trials (not shown here). The fitting results (also carried out by PSO technique) using the models given by (2) (denoted "exp" in the legend), (6) ("CC"), (15) ("DC"), (20) ("HN"), (24) ("q-exp") and (37) ("logistic") are also shown. The models' parameters are given in the figure caption. We also plotted the normalized error versus time and in box plot format for the different models. It is clear from Fig. 3 that the exponential decay model [see (2)] is the least efficient in properly capturing the
Fig. 3. Plots of (a) normalized voltage and (d) normalized charge versus time measured on a precharged commercial Samxon supercapacitor (part No. DRL105S0TF12RR, rated 2.7 V, 1 F) when connected to a resistive load of 2 Ω. Fitting results for voltage/charge, respectively, using (2) (“exp” with \( \tau = \{6.092, 10.92\} \) s), (6) (“CC” with \( \tau_{x,\alpha} = \{5.750 \text{ s}, 0.946\}, \{8.698 \text{ s}, 0.800\} \)), (15) (“DC” with \( \tau_{x,\beta} = \{8.296 \text{ s}, 0.760\}, \{26.00 \text{ s}, 0.496\} \)), (20) (“HN” with \( \tau_{x,\alpha,\beta} = \{6.709 \text{ s}, 0.984, 0.888\}, \{8.689 \text{ s}, 0.802, 1.000\} \)), (24) (“q-exp” with \( \tau_{x,\alpha} = \{5.144 \text{ s}, 1.221\}, \{5.829 \text{ s}, 1.822\} \)), and (37) (“logistic” with \( \tau_{x,\alpha} = \{8.843 \text{ s}, 0.141\}, \{18.00 \text{ s}, −0.319\} \)) are also shown. Normalized errors plotted versus time (b) and (e) and in box plot format (c) and (f) for the different models are presented for voltage and charge, respectively.

The experimental data of the nonideal, dissipative EDLC device. The RMSE for the (normalized) voltage and charge fitting is found to be 0.016 and 0.065, respectively. We also remark that the fitting time constant \( \tau \) for the voltage is 6.092 s, whereas for the charge it is 10.92 s. This indicates that the relation \( q(t) = C v(t) \) where \( C \) is a constant capacitance is not valid for nonideal capacitive devices [6], [7], [8], [44]. Fractional-order and \( q \)-deformed exponential models, on the other hand, whether they are with one or more extra degrees of freedom are evidently more appropriate at closely following the nonexponential data. The RMSE associated with the models of (6), (15), (20), (24), and (37) is 0.005, 0.007, 0.004, 0.006, and 0.008, respectively, for voltage fitting and 0.015, 0.039, 0.015, 0.012, and 0.046, respectively, for charge fitting. In particular, for both the voltage and charge profiles, it seems like the Cole–Cole-based model [see (6)] and its generalization to the Havriliak–Negami model [see (20)] are the best performing fractional-order models for this case. The \( q \)-exponential model [see (24)] with \( q \neq 1 \) has proved to be equally reliable too as indicated from the error of regressions and their plots.

However, the evolution kinetic equation for \( \rho(t) \) given by (23) in which the local time derivative of \( \rho(t) \) is proportional to a power of \( \rho(t) \) is physically more tractable than the fractional-order equations (10) or (12) for the Cole–Cole model or (22) for the Havriliak–Negami model. As illustrated schematically in Fig. 1, the nonlocal (global) integro-differential fractional models require knowledge of all the events over the history of the device to estimate its current state at an instant \( t \) [23], [24], [25], [26]. Even though the long-term memory effect tends to fade away quickly compared with the short term, it is still a challenging task to gather all prior state information about a device described with the fractional-order models. It is worth mentioning again that the \( q \)-exponential function is directly connected to the nonadditive Tsallis entropy [32] and to Beck and Cohen’s superstatistics [45], which makes its physical interpretation easier to justify. Finally, we note that for the time-domain analysis, the \( q \)-exponential function has a simple algebraic form, and thus more efficient to compute compared with the cumbersome series associated with the ML and the \( H \)-functions that appear in the solutions of fractional-order equations. This is the opposite of what we have seen with the fitting models of the impedance data. The fractional impedance models are simple fractions with one or two power coefficients, whereas the \( q \)-parameterized models involving the incomplete gamma function or the hypergeometric series are numerically more demanding to compute.

VI. Conclusion

In this work, we reviewed different ways of generalizing the evolution equation given by (3) by first replacing the first-order time derivative \( d\rho(t)/dt \) with different forms of fractional-order derivatives leading to the well-known
We then proposed a new model in which $\rho(t)$ in (3) is replaced by a power function, i.e., $[\rho(t)]^q (q \in \mathbb{R})$, which can also be expressed in terms of a linear $q$-deformed derivative. This led to a relaxation function in terms of the $q$-exponential function able to capture quite efficiently the nonexponential behavior observed with a commercial nonideal (dissipative) EDLC device. The model can also be interpreted from a superstatistic point of view [45] as representing the collective response of the superposition of a large number of spatially distributed network of subsystems, each of which follows the traditional exponential decay. The dual nonlinear $q$-derivative led to a logistic function type of decay. The corresponding $q$-parameterized impedance functions, involving the incomplete gamma function or the hypergeometric function, are also fitted to the experimental data of EDLC and compared with the traditional fractional-order models. All the non-RC models, given their extra degrees of freedom, are capable of capturing the time-domain and frequency-domain data with great fidelity. However, the fractional-order models are found to be computationally more efficient with impedance fitting, whereas the $q$-parameterized models are more efficient with the time-domain relaxation data. In addition, as we noted the $q$-deformed evolution equations maintain the first-order evolution of the evolving function and are directly associated with the Tsallis thermostatistics and Beck and Cohen's superstatistics, which makes its physical comprehension less complicated than the nonlocal, fractional-order integro-differential evolution equations.

**APPENDIX**

**Fox's H-Function**

Fox's $H$-function is defined in terms of Mellin–Barnes-type integral as [46]

$$H_{m,n}^{p,q}(z) = \frac{1}{2\pi i} \int_L h(s)z^{-s} ds$$

where $h(s)$ is given by

$$h(s) = \frac{\left\{ \prod_{j=1}^{p} \Gamma(b_j + B_j s) \right\} \left\{ \prod_{j=1}^{q} \Gamma(1 - \alpha_j - A_j s) \right\} \left\{ \prod_{j=1}^{m} \Gamma(1 - b_j - B_j s) \right\} \left\{ \prod_{j=1}^{n} \Gamma(1 - a_j + A_j s) \right\}}{\left\{ \prod_{j=1}^{p} \Gamma(1 - b_j - B_j s) \right\} \left\{ \prod_{j=1}^{q} \Gamma(1 - a_j + A_j s) \right\}}$$

where $i = (-1)^{1/2}$, $m, n, p, q$ are the integers satisfying $(0 \leq n \leq p, 1 \leq m \leq q)$, $\zeta \neq 0$, and $z^{-t}$ is $\exp[-s(\ln |z| + i \arg z)]$, $A_j, B_j \in \mathbb{R}$, $a_j, b_j \in \mathbb{R}$ or $\mathbb{C}$ with $(i = 1, \ldots, p)$, $(j = 1, \ldots, q)$. The contour of integration $L$ is a suitable contour separating the poles $-(b_j + v)/B_j$, $(j = 1, \ldots, m; v = 0, 1, 2, \ldots)$, of the gamma functions $\Gamma(b_j + B_j s)$ from the poles $(1 - a_j + k)/A_j$, $(\lambda = 1, \ldots, n; k = 0, 1, 2, \ldots)$ of the gamma functions $\Gamma(1 - a_j - A_j s)$, that is $A_j(b_j + v) \neq B_j(a_j - k + 1)$. An empty product is always interpreted as unity.

A comprehensive account of the $H$-function is available in the work of Mathai et al. [46] and [47].

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