

Theoretical Verification of the Formula of Charge function in Time of Capacitor ($q = c * v$) For Few Cases of Excitation Voltage

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Abstract

We have developed and derived a formula for capacitor i.e. charge as a function of time, which is convolution operation of time varying capacity function and time-varying voltage function. This is different to the usual and conventional way of writing capacitance multiplied by voltage to get charge stored in a capacitor. This new deliberation with convolution operation works well for classical capacitors (i.e. ideal loss less capacitors), that is of a constant capacity at all frequencies, and also for a time varying capacity function given by decaying power-law: that gives the formation of a fractional capacitor. In this paper, we use this developed new charge storage expression and apply to various types of inputs excitation voltage-sinusoidal, step, ramp voltage and then analyze and interpret the results for charge stored, the current expressions, the loss-tangent and the memory effects. With this new formulation, we also evaluate impedance function of a classical capacitor as well as a fractional capacitor, and also elaborate on the Nyquist's diagram, that is employed to study various dielectric materials via impedance spectroscopy. This new approach of charge storage concept is yet to be practically as well as theoretically applied-though some initial work has started. This paper gives a theoretical validity test i.e. analytically obtained in several applications for this new formulation, of charge storage formula. This paper will be useful in various super-capacitor studies, dielectric relaxation experiments, and impedance spectroscopy for various material developments for electrical energy storage missions; however, this concept is yet to be used to its full potential.

Keywords

Capacity Function, Fractional Capacitor, Fractional Derivative, Convolution, Laplace Transform, Memory Effect, Nyquist's diagram, Curie-von Schweidler law, loss tangent

1. Introduction

The new formulation of charge function in time is $q(t) = c(t) * v(t)$ derived in detail; with $c(t)$ for ideal loss less capacitor case, as well as time varying capacity function (fractional capacitor) case in [1]. The operation (*) is the convolution operator [1]. The capacity function $c(t)$ is the function which decays with time, and has the form of singular power law $c(t) \propto t^{-\alpha}$; $0 < \alpha < 1$ and this acts only at the time of application of voltage change $v(t)$. For ideal case of loss-less capacitor the capacity function is $c(t) \propto \delta(t)$; [1]. We will use this formula $q(t) = c(t) * v(t) = \int_0^t c(t-\tau)v(\tau)d\tau$ and discuss various cases for $v(t)$ as sinusoidal voltage excitation, step voltage excitation, ramp voltage excitation. We give interpretations for all the theoretical derived results with this new approach and will verify the results in each case. We will use the memory-effect [6], [7], [14], [15] using this new formulation; which can only be

observed for a case of fractional capacitor. In this paper we will always take the exponent, α , in the power-law decaying capacity function, $c(t) \propto t^{-\alpha}$ to be between zero and one: $0 < \alpha < 1$.

This power-law decay function is singular at $t = 0$ and is consistent with the singular power-law-decay relaxation current given by the Universal Dielectric Response (UDR) of Curie, von Schweidler & Jonscher[2]-[5]. The use of this universal dielectric relaxation (UDR) law gives current voltage relation of a capacitor as given by fractional derivative [6]-[10]; i.e. $i(t) \propto D_t^\alpha v(t)$. The non-singular decaying function for $i(t)$ and $c(t)$ gives all together different form of current voltage relations for capacitor is discussed in [11], [39]. There is lot of pioneering work dealing with usage of non-singular functions in various system dynamics studies [23]-[36]. In this paper we will deal with singular function as response function in $c(t) \propto t^{-\alpha}$, and $i(t) \propto t^{-\alpha}$ as per universal dielectric relaxation law of Curie-von Schweidler.

We note a priori that the constant C_α is proportionality constant for power-law capacity function i.e. $c(t) \propto t^{-\alpha}$ and not 'fractional capacity' for fractional capacitor. The 'fractional capacity' of a fractional capacitor we will represent in this paper as $C_{F-\alpha}$ which has units of Farad / $\text{sec}^{1-\alpha}$ [1], [6], [7], [15]. We assume that the fractional capacitor has no resistance, (like ideal capacitor has no resistance) and is excited by ideal voltage source (having output impedance as zero). We will use Laplace Transform technique in all analysis to get stored charge expression $q(t)$ and then the current $i(t)$. In all the cases in subsequent sections, we will apply this new formula i.e. $q(t) = c(t) * v(t)$ and give the validity justification by interpretations of the result. The voltage, $v(t)$ across a capacitor or dielectric changes at a rate in proportion to the current: $i(t) = D_t^1 (c(t) * v(t))$, with $c(t) = C_\alpha t^{-\alpha}$ we get $i(t) = (c(t))(v(0)) + c(t) * D_t^1 v(t)$ [1]. This relaxation law is detailed in [1], for ideal capacitor as well as fractional capacitor; derived from $q(t) = c(t) * v(t)$. The time varying capacity function $c(t)$ is the one that defines the response function; and by principle of causality we write $q(t) = c(t) * v(t)$; where $v(t)$ is the input impressed voltage. The operation (*) is the convolution operation [1]. This is contrary to usual usage of formula i.e. $q(t) = c(t)v(t)$ where the product of the two is used.

This paper is organized as several sections. Section-2 deals with use of formula $q(t) = c(t) * v(t)$ for input $v(t)$ as sinusoidal excitation, and interpretations for classical capacitor and fractional capacitor, results of phase angle, and loss-tangent. Section-3 deals with use of $q(t) = c(t) * v(t)$, to have impedance expression $Z(s)$ for classical capacitor and fractional capacitor. Section-4 describes the impedance function obtained from $q(t) = c(t) * v(t)$ used to interpret Nyquist's plot for a fractional capacitor, and to extract the values of fractional capacity $C_{F-\alpha}$ in units of Farads / $\text{sec}^{1-\alpha}$, and interpretations. Section-5 deals with usage of the formula $q(t) = c(t) * v(t)$ for a step input excitation, while Section-6 describes the memory effect that we interpret from Section-5. The Section-7 deals with excitation $v(t)$ as ramp-voltage. In the Section-8 we compare the charge $q(t)$ for the cases of step input and ramp input. In Section-9 we have discussion on the observations and inferences of the paper, followed by Conclusion References and Acknowledgement. We reiterate this new formula is still not widely used anywhere for theoretical or practical studies. However in a recent study [40] the validation of this new formulation $q(t) = c(t) * v(t)$ via experimentation is carried out. This paper is made from

presentations and deliberations for the project [37]. We plan to use this new concept in studies of charge storage in super-capacitor as continuation of the project [37].

2. Charge storage by sinusoidal voltage excitation to a fractional capacitor and ideal capacitor

2-a. Excitation by voltage signal as cosine function

Sinusoidal voltage of cosine wave form is applied to an uncharged capacitor. We write $v(t) = V_m \cos \omega_0 t$, at time $t=0$. Then charge function in time is given as convolution operation for a time varying capacity function described as $c(t) = C_\alpha t^{-\alpha}$, $0 < \alpha < 1$ for a fractional capacitor as following

$$q(t) = c(t) * v(t) = (C_\alpha t^{-\alpha}) * (V_m \cos \omega_0 t) \quad (1)$$

We note that the capacity function in the form i.e. $c(t) = C_\alpha t^{-\alpha}$, implies a fractional capacitor that is given by $i(t) \propto D_t^\alpha v(t)$, (where D_t^α is fractional derivative of order α w.r.t. variable t) i.e. the relation of current and voltage via fractional derivative [6]-[10]. For classical ideal capacitor we have $i(t) \propto D_t^1 v(t)$. We apply Laplace Transform to the above Eq. (1) and write the following

$$\mathcal{L}\{q(t)\} = \mathcal{L}\{c(t) * v(t)\}; \quad Q(s) = (C(s))(V(s)) \quad (2)$$

In Eq. (2) we have $C(s) = \mathcal{L}\{C_\alpha t^{-\alpha}\} = C_\alpha \Gamma(1-\alpha) s^{-(1-\alpha)}$ and $V(s) = \mathcal{L}\{V_m \cos \omega_0 t\} = \frac{V_m s}{s^2 + \omega_0^2}$.

This gives $Q(s)$ as follows

$$\begin{aligned} Q(s) &= \left(\frac{C_\alpha \Gamma(1-\alpha)}{s^{1-\alpha}} \right) \left(\frac{V_m s}{s^2 + \omega_0^2} \right) = \frac{V_m C_\alpha \Gamma(1-\alpha)}{\omega_0} \left(s^\alpha \frac{\omega_0}{s^2 + \omega_0^2} \right) \\ &= \frac{V_m C_\alpha \Gamma(1-\alpha)}{\omega_0} \left(\mathcal{L}\{D_t^\alpha \sin \omega_0 t\} \right) \end{aligned} \quad (3)$$

In above steps of Eq. (3) we used Laplace Transform of Fractional Derivative as $\mathcal{L}\{D_t^\alpha f(t)\} = s^\alpha F(s)$ with $f(0) = 0$ and $0 < \alpha < 1$ [10], [12], [13] and $\mathcal{L}\{\sin at\} = \frac{a}{s^2 + a^2}$. Taking the inverse Laplace transform of the above Eq. (3), we get the following

$$q(t) = \frac{V_m C_\alpha \Gamma(1-\alpha)}{\omega_0} (D_t^\alpha \sin \omega_0 t) = \frac{V_m C_{F-\alpha}}{\omega_0} (D_t^\alpha \sin \omega_0 t) \quad (4)$$

Here in Eq. (4) we have introduced a constant $C_{F-\alpha} = C_\alpha \Gamma(1-\alpha)$ as fractional capacity in units of Farad / sec^{1- α} [1], [6], [7], [8], [9], [11]; this we will elaborate later subsequently. We have fractional derivative of $\sin(x)$ as following [12], [13]

$$D_x^\alpha \sin(x) = \frac{d^\alpha \sin(x)}{dx^\alpha} = \sin\left(x + \frac{\alpha\pi}{2}\right) + \frac{x^{-1-\alpha}}{\Gamma(-\alpha)} - \frac{x^{-3-\alpha}}{\Gamma(-\alpha-2)} + \dots \quad (5)$$

We note that symbol $D_x^\alpha f(x)$ is written as $d^\alpha f(x) / dx^\alpha$ in Eq. (5). We write $x = \omega_0 t$ thus we have $dx = \omega_0 dt$ that gives $(dt)^\alpha = \omega_0^{-\alpha} dx$. With this substitution in Eq. (5) we write the following from Eq. (4)

$$q(t) = \frac{V_m C_{F-\alpha}}{\omega_0} \frac{d^\alpha \sin(\omega_0 t)}{dt^\alpha} = \frac{V_m C_{F-\alpha}}{\omega_0^{1-\alpha}} \left(\sin\left(\omega_0 t + \frac{\alpha\pi}{2}\right) + \frac{(\omega_0 t)^{-1-\alpha}}{\Gamma(-\alpha)} - \frac{(\omega_0 t)^{-3-\alpha}}{\Gamma(-\alpha-2)} + \dots \right) \quad (6)$$

The transient terms i.e. $t^{-1-\alpha}$, $t^{-3-\alpha}$, ... ($0 < \alpha < 1$) in the Eq. (6) expression decays to zero for large times (as in limit $t \uparrow \infty$). Thus we write the steady state charge function from Eq. (6) as following

$$q(t) = V_m C_{F-\alpha} \omega_0^{\alpha-1} \sin\left(\omega_0 t + \frac{\alpha\pi}{2}\right) \quad (7)$$

From Eq. (7) we get the steady state current as following

$$i(t) = \frac{dq(t)}{dt} = \frac{d}{dt} \left(V_m C_{F-\alpha} \omega_0^{\alpha-1} \sin\left(\omega_0 t + \frac{\alpha\pi}{2}\right) \right) = V_m C_{F-\alpha} \omega_0^\alpha \cos\left(\omega_0 t + \frac{\alpha\pi}{2}\right) \quad (8)$$

This Eq. (8) shows at steady state the current in fractional capacitor leads the voltage by angle $\alpha\pi/2$. This is true and also this is a practical way to validate experimentally a fractional integrator or differentiator circuits, by sinusoidal input [10]. The leading current is $\pi/2$ to voltage excitation for ideal loss less capacitor where ($\alpha = 1$). This result we obtained by use of $q(t) = c(t) * v(t)$.

In the following steps to re-write above Eq. (8)

$$\begin{aligned} q(t) &= V_m C_\alpha \Gamma(1-\alpha) \omega_0^{\alpha-1} \sin\left(\frac{\pi}{2} + \left(\omega_0 t - \frac{\pi}{2} + \frac{\alpha\pi}{2}\right)\right) \\ &= V_m C_\alpha \Gamma(1-\alpha) \omega_0^{\alpha-1} \cos\left(\omega_0 t - \frac{(1-\alpha)\pi}{2}\right) = Q_p \cos\left(\omega_0 t - \frac{(1-\alpha)\pi}{2}\right) \\ Q_p &= V_m C_\alpha \Gamma(1-\alpha) \omega_0^{\alpha-1} = V_m C_{F-\alpha} \omega_0^{\alpha-1} \end{aligned} \quad (9)$$

We observe in Eq. (9) $q(t) = Q_p \cos(\omega_0 t - \phi)$ that charge-function $q(t)$ lags voltage function $v(t)$ at steady state by angle $\phi = \frac{(1-\alpha)\pi}{2}$.

From Eq. (9) we see for $\alpha = 1$ i.e. for ideal capacitor there is no phase difference ϕ (lag) between charge function and voltage function [1]. This is for ideal loss less capacitor where capacity function is $c(t) = C_1\delta(t)$; [1] and we have $\phi = 0$. This we verify by using $q(t) = c(t) * v(t)$, for ideal capacitor $c(t) = C_1\delta(t)$. We get $Q(s) = (\mathcal{L}\{C_1\delta(t)\})(\mathcal{L}\{V_m \cos \omega_0 t\}) = V_m C_1 \frac{s}{s^2 + \omega_0^2}$. Then we get $q(t) = V_m C_1 \cos \omega_0 t = Q_m \cos \omega_0 t$, that is in same phase with voltage function $v(t)$; [1], with $\phi = 0$.

2-b. Excitation by voltage signal as sine function

Let a sinusoidal voltage be applied to an uncharged capacitor $v(t) = V_m \sin \omega_0 t$, at time $t = 0$ for a fractional capacitor given by capacity function $c(t) = C_\alpha t^{-\alpha}$. We write charge $q(t)$ by using the formula $q(t) = c(t) * v(t)$ as following

$$q(t) = c(t) * v(t) = (C_\alpha t^{-\alpha}) * (V_m \sin \omega_0 t) \quad (10)$$

We apply Laplace Transform to the above and write the following

$$\mathcal{L}\{q(t)\} = \mathcal{L}\{c(t) * v(t)\}; \quad Q(s) = C(s)V(s) \quad (11)$$

We have $C(s) = \mathcal{L}\{C_\alpha t^{-\alpha}\} = C_\alpha \Gamma(1-\alpha) s^{-(1-\alpha)}$ and $V(s) = \mathcal{L}\{V_m \sin \omega_0 t\} = \frac{V_m \omega_0}{s^2 + \omega_0^2}$. This gives $Q(s)$ as follows

$$\begin{aligned} Q(s) &= \left(\frac{C_\alpha \Gamma(1-\alpha)}{s^{1-\alpha}} \right) \left(\frac{V_m \omega_0}{s^2 + \omega_0^2} \right) = V_m C_\alpha \Gamma(1-\alpha) \left(s^{\alpha-1} \frac{\omega_0}{s^2 + \omega_0^2} \right) \\ &= V_m C_\alpha \Gamma(1-\alpha) \left(\mathcal{L}\{D_t^{\alpha-1} \sin \omega_0 t\} \right) \end{aligned} \quad (12)$$

In above Eq. (12) we used Laplace Transform of Fractional Derivative for $0 < \alpha < 1$ as $\mathcal{L}\{D_t^\alpha f(t)\} = s^\alpha F(s)$ with $f(0) = 0$ [10], [12], [13] and $\mathcal{L}\{\sin at\} = \frac{a}{s^2 + a^2}$. Taking the inverse Laplace transform of the Eq. (12), we get the following

$$q(t) = V_m C_\alpha \Gamma(1-\alpha) (D_t^{\alpha-1} \sin \omega_0 t) \quad (13)$$

From the formula as noted above Eq. (5) for $D_x^\alpha \sin x$ we get by replacing α with $\alpha - 1$ the following

$$D_x^{\alpha-1} \sin(x) = \frac{d^{\alpha-1} \sin(x)}{dx^{\alpha-1}} = \sin\left(x + \frac{(\alpha-1)\pi}{2}\right) + \frac{x^{-1-(\alpha-1)}}{\Gamma(-(\alpha-1))} - \frac{x^{-3-(\alpha-1)}}{\Gamma(-(\alpha-1)-2)} + \dots \quad (14)$$

Since $0 < \alpha < 1$ and for limit $x \uparrow \infty$ the terms in Eq. (14) i.e. $x^{-1-(\alpha-1)}$, $x^{-3-(\alpha-1)}$... goes to zero, and we write, the following for large x , the steady state solution

$$D_x^{\alpha-1} \sin(x) = \frac{d^{\alpha-1} \sin(x)}{dx^{\alpha-1}} = \sin\left(x + \frac{(\alpha-1)\pi}{2}\right) \quad (15)$$

With change of variables as $x = \omega_0 t$, we have $(dx)^{\alpha-1} = \omega_0^{\alpha-1} (dt)^{\alpha-1}$, we write the following

$$\frac{d^{\alpha-1} \sin(x)}{dx^{\alpha-1}} = \frac{1}{\omega_0^{\alpha-1}} \frac{d^{\alpha-1} \sin(\omega_0 t)}{dt^{\alpha-1}} = \sin\left(\omega_0 t + \frac{(\alpha-1)\pi}{2}\right) \quad (16)$$

Using $D_t^{\alpha-1} \sin(\omega_0 t) = \omega_0^{\alpha-1} \sin\left(\omega_0 t + \frac{(\alpha-1)\pi}{2}\right)$ from Eq. (16) we write steady state charge as follows

$$\begin{aligned} q(t) &= V_m C_\alpha \Gamma(1-\alpha) \left(\frac{d^{\alpha-1} \sin(\omega_0 t)}{dt^{\alpha-1}} \right) = V_m C_\alpha \Gamma(1-\alpha) \omega_0^{\alpha-1} \sin\left(\omega_0 t + \frac{(\alpha-1)\pi}{2}\right) \\ &= V_m C_{F-\alpha} \omega_0^{\alpha-1} \sin\left(\omega_0 t - \frac{(1-\alpha)\pi}{2}\right) \end{aligned} \quad (17)$$

The charge $q(t)$ lags the voltage function $v(t)$ by an angle $\frac{(1-\alpha)\pi}{2}$. We differentiate Eq. (17) and write the current as follows

$$\begin{aligned} i(t) &= \frac{dq(t)}{dt} = V_m C_{F-\alpha} \omega_0^{\alpha-1} \omega_0 \cos\left(\omega_0 t - \frac{(1-\alpha)\pi}{2}\right) = V_m C_{F-\alpha} \omega_0^\alpha \cos\left(\omega_0 t - \frac{\pi}{2} + \frac{\alpha\pi}{2}\right) \\ &= V_m C_{F-\alpha} \omega_0^\alpha \sin\left(\omega_0 t + \frac{\alpha\pi}{2}\right) \end{aligned} \quad (18)$$

The current leads voltage by angle $\frac{\alpha\pi}{2}$ for fractional capacitor.

2-c. Interpretation of the sinusoidal analysis

From Eq. (9) we see that $\phi = \frac{(1-\alpha)\pi}{2}$. The lagging phase angle of charge function $q(t)$ is time invariant or a constant, for a fractional capacitor, if we assume α constant. In [6], [7] it is discussed that loss tangent of a fractional capacitor, that follows Curie-von Schweidler law of dielectric relaxation; is $\tan \frac{(1-\alpha)\pi}{2}$, that is derived from sinusoidal analysis of transfer function of fractional capacitor, taking phase angle of lagging voltage to a sinusoidal current applied. This loss tangent is frequency independent quantity; implying loss per cycle is **the** same fraction of stored energy at all frequencies of $v(t) = V_m \cos \omega_0 t$, $0 \leq \omega_0 < \infty$ [6], [7].

We have observation Eq. (9) of time invariant phase lag of $q(t)$ for a sinusoidal input excitation. This may be a new definition of loss tangent, which is loss tangent of a dielectric is the tangent of phase lag angle ϕ of charge function $q(t)$ w.r.t. $v(t)$. We are just proposing this definition here, and in **the** future study we will try and relate to Electromagnetic Theory of loss tangent concept in dielectrics by using $q(t) = c(t) * v(t)$. But the point we make here, that we obtained invariant

loss tangent as $\tan \frac{(1-\alpha)\pi}{2}$ from Eq. (9) by use of $q(t) = c(t) * v(t)$ for a fractional capacitor. The loss tangent for ideal loss less capacitor $\alpha = 1$ is zero.

We note that for a time varying capacity function $c(t) = C_\alpha t^{-\alpha}$, (a fractional capacitor) with $0 < \alpha < 1$ the charge function is $q(t) = Q_p \cos(\omega_0 t - \phi)$. The peak value of charge $Q_p = V_m C_{F-\alpha} \omega_0^{\alpha-1}$ varies with operating frequency ω_0 of the excitation voltage i.e. $v(t) = V_m \cos \omega_0 t$. With parameters $C_{F-\alpha}$ and α assuming to be constant with varying ω_0 , and V_m as the maximum rated value of the operational circuit; the peak charge Q_p Eq. (9) decreases as ω_0 the input excitation frequency is increased. While for ideal loss less capacitors the peak charge $Q_m = V_m C_1$ remains invariant with the frequency of input voltage. Therefore, with various input excitation voltage-wave-forms of various frequencies we will be getting different peak charge values, though the excitation voltage is within the capacitor maximum rating V_m . This implies that a square wave, a triangular wave, a trapezoidal wave of voltage-excitation, with $|v(t)|_{\max} = V_m$ will be giving different peak charge Q_p stored, as they will be having different harmonic frequencies. For example a square wave voltage of positive and negative cycles, a symmetric triangular wave voltage, and a pure sinusoidal with the same period and with $|v(t)|_{\max} = V_m$ will have different peak charge Q_p stored. However, the assumption $C_{F-\alpha}$ and α to be constant with varying ω_0 , does not hold, that we will explain in Nyquist's diagram shortly.

We thus obtained all above observations and interpretations for sinusoidal excitation by using the new formula i.e. $q(t) = c(t) * v(t)$; applied for an ideal as well as fractional capacitor. The similar interpretation and observations as described here for $v(t) = V_m \cos \omega_0 t$ in this section is also obtained for $v(t) = V_m \sin \omega_0 t$; Eq. (10) to Eq. (18).

3. Impedance Expression of Fractional Capacitor

We have the relation of charge function as $q(t) = c(t) * v(t)$. By differentiation of this expression [1] we get current through capacitor as following

$$i(t) = \frac{dq(t)}{dt} = c(t) * \frac{dv(t)}{dt} = \int_0^t c(t-\tau) \left(\frac{dv(\tau)}{d\tau} \right) d\tau \quad (19)$$

Taking Laplace Transform of the above Eq. (19) we obtain $I(s) = (\mathcal{L}\{c(t)\})(sV(s))$. The impedance is defined as $Z(s) = V(s) / I(s)$. From this we write, for the capacity function $c(t)$ of capacitor, the impedance function $Z(s)$ in Laplace domain as

$$Z(s) = \frac{1}{s(\mathcal{L}\{c(t)\})} \quad (20)$$

We note that Eq. (20) is a new way of expressing impedance function that we got from $q(t) = c(t) * v(t)$. For ideal loss less capacitor with $c(t) = C_1 \delta(t)$; [1] we get the classical impedance formula i.e.

$$Z(s) = \frac{1}{s\mathcal{L}\{C_1\delta(t)\}} = \frac{1}{sC_1} \quad (21)$$

With $s = j\omega$ where $j = \sqrt{-1}$ we write for sinusoidal case the impedance function as following

$$Z(\omega) = \frac{1}{j\omega C_1} = -\frac{j}{\omega C_1} \quad (22)$$

For a capacitor having time varying capacity function as $c(t) = C_\alpha t^{-\alpha}$, (i.e. a fractional capacitor) we get

$$\begin{aligned} Z(s) &= \frac{1}{s\mathcal{L}\{C_\alpha t^{-\alpha}\}} = \frac{1}{s(C_\alpha \Gamma(1-\alpha) s^{\alpha-1})} \\ &= \frac{1}{s^\alpha C_\alpha \Gamma(1-\alpha)} = \frac{1}{s^\alpha C_{F-\alpha}}; \quad C_{F-\alpha} = C_\alpha \Gamma(1-\alpha) \end{aligned} \quad (23)$$

From above Eq. (23) we get $I(s) = C_\alpha \Gamma(1-\alpha) (s^\alpha V(s))$. Using the Laplace transforms of fractional derivative i.e. $\mathcal{L}\{D_t^\alpha f(t)\} = s^\alpha F(s)$ with $f(0) = 0$ and $0 < \alpha < 1$ we get the following

$$i(t) = C_{F-\alpha} \frac{d^\alpha v(t)}{dt^\alpha}; \quad C_{F-\alpha} = C_\alpha \Gamma(1-\alpha) \quad (24)$$

We note that the constant $C_{F-\alpha}$ has unit of Farad / sec $^{1-\alpha}$ that is unit for fractional capacitor.

With $s = j\omega$ we obtain the following

$$Z(s) = \frac{1}{C_\alpha \Gamma(1-\alpha)} (j\omega)^{-\alpha} = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \left(\cos \frac{\alpha\pi}{2} - j \sin \frac{\alpha\pi}{2} \right) \quad (25)$$

We have $\text{Re } Z(\omega) = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \cos \frac{\alpha\pi}{2}$ and $-\text{Im } Z(\omega) = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \sin \frac{\alpha\pi}{2}$.

4. The Nyquist's diagram of a fractional capacitor

The impedance spectroscopy gives Nyquist's diagram, when $X = \text{Re } Z(\omega)$ and $Y = -\text{Im } Z(\omega)$ is plotted with frequency ω varying from 0 to ∞ in X-Y plane [41]. For ideal loss less capacitor with capacity function as $c(t) = C_1 \delta(t)$, the Nyquist diagram is just Y-Axis in units of Ω , with $Y = (\omega C_1)^{-1} \Omega$ and $X = 0 \Omega$. When in limit $\omega \downarrow 0$ then $Y \uparrow \infty$ and while at very-very high frequency i.e. in limit $\omega \uparrow \infty$, we have $Y \downarrow 0$; with $X = 0$ at all frequencies. The capacitance C_1 is constant at all frequencies. For ideal loss less capacitors we have equivalent series resistance (ESR) as 0Ω at all frequencies.

For a fractional capacitor with time varying capacity function as $c(t) = C_\alpha t^{-\alpha}$, we have $X = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \cos \frac{\alpha\pi}{2} \Omega$ and $Y = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \sin \frac{\alpha\pi}{2} \Omega$. We have a slope of the Nyquist's diagram as $\tan \frac{\alpha\pi}{2}$. When $\alpha \approx 1$, the angle of slope is tending to 90° (i.e. the Nyquist's diagram tends towards as vertical line parallel to Y-Axis). While $\alpha = 0.5$, the slope is one, the angle of the slope is 45° . We remark here that when $\alpha = 0.5$ is Warburg Impedance region [10], [41]. Then at still higher frequencies ω , there is a semi-circular region-that is related to charge-transfer Faradic region (charge-transfer zone) [41], finally that ends at $Y = 0 \Omega$ and $X \approx 0 \Omega$. This fractional

capacitor phenomenon is observed nicely in the super-capacitors. The Figure-1 gives several Nyquist's diagrams for different super-capacitors made indigenously for trial-and being tested via impedance spectroscopy [37]. In this paper we are not discussing the Electro-Chemical aspects and material science aspects via results of Impedance Spectroscopy of the super-capacitor, rather trying to develop the explanation for Nyquist's diagram using our formula $q(t) = c(t) * v(t)$.

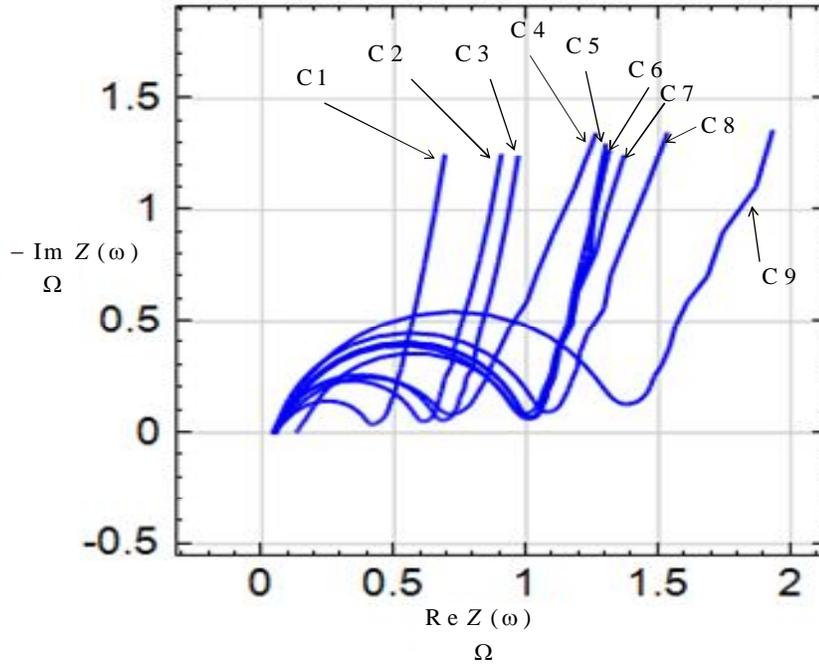


Figure-1: Nyquist's diagram of Impedance Spectroscopy for nine super-capacitors proto types under development

The Figure-1 is recent result for our testing of indigenous capacitors developed [37] that we are making en-mass for characterization-and certification of our developed process. This work we are doing since long [38], now it is matured for industrial usage.

From the Figure-1 we redraw Figure-2, for only one sample C1, for our calculations and explanation. The capacitor with time varying capacity function as $c(t) = C_\alpha t^{-\alpha}$, (fractional capacitor) has ESR as $R_s = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \cos \frac{\alpha\pi}{2} \Omega = X$. This R_s is a function of frequency ω . At very-very high frequency $\omega \uparrow \infty$, this ESR is low value ($\sim 0.2\Omega$) and at very-very low frequency $\omega \downarrow 0$ this ESR is at high value ($\sim 0.9\Omega$); see Figure-2.

The imaginary part is capacitive impedance (reactive impedance) in Ω , i.e. $Y = \frac{1}{C_\alpha \omega^\alpha \Gamma(1-\alpha)} \sin \frac{\alpha\pi}{2} \Omega$. This is also a frequency (ω) dependent. The value of $Y \uparrow \infty$ for very-very low frequency, while the value of $Y \downarrow 0$ at very-very high frequency; as depicted in Figure-2.

We show in Figure-2 the Warburg region, at around frequency 0.14Hz, $\omega = 0.88$ Radians / sec, shown as point P. At this point P we have ESR as $R_s = 0.62\Omega$. At this point P of frequency we have $\alpha = 0.5$, and $Y = 0.3\Omega$.

Therefore at this point P we have

$$C_{F-\alpha} = C_{\alpha} \Gamma(1-\alpha) = \frac{1}{Y\omega^{\alpha}} \sin \frac{\alpha\pi}{2} = \frac{\sin 45^{\circ}}{0.3 \times (0.88)^{0.5}} = 2.51 \text{Farad} / \text{sec}^{0.5}.$$

This Warburg region with $\alpha \approx 0.5$ remains for several high frequencies until the Faradic (charge-transfer) region of semi-circular bulge is observed [41]. Thus at various points of frequency ω of Nyquist's diagram, we get the value of α , ESR (R_s), and Fractional capacity $C_{F-\alpha}$.

We observe, that at very low frequency 0.006Hz, $\omega \approx 0.04$ Radians/sec the Y value tends towards 1Ω . Here we take α as 0.9. Therefore we have $C_{F-\alpha} \cong \frac{\sin 81^{\circ}}{1 \times (0.04)^{0.9}} = 18 \text{Farad} / \text{sec}^{0.1}$. In the limit that is $\alpha \approx 1.0$ and at this point we get $C_{F-\alpha} \Big|_{\alpha \approx 1.0} \approx 25 \text{Farad}$, with $R_s = 0.9\Omega$.

This impedance Nyquist's diagram says that we have equivalent circuit representing capacitor with time varying capacity function $c(t) = C_{\alpha} t^{-\alpha}$; as series connected ESR R_s with Fractional Capacitor $C_{F-\alpha}$ (Farad/sec $^{1-\alpha}$), with $C_{F-\alpha} = C_{\alpha} \Gamma(1-\alpha)$ as dependent on ω . As interesting observation, what we got a component R_s that gives resistive losses for super-capacitor, though we assumed in our analysis that the ideal voltage source is directly connected to our capacitor without any resistance. The $C_{F-\alpha}$ component with α as we discussed gives charge-discharge efficiency [18], and the parameters R_s and $C_{F-\alpha}$ are extracted by constant current charge discharge excitation (that aspect we are not discussing in this paper).

Here we have explained the Nyquist's diagram of fractional capacitor by using the formula $q(t) = c(t) * v(t)$.

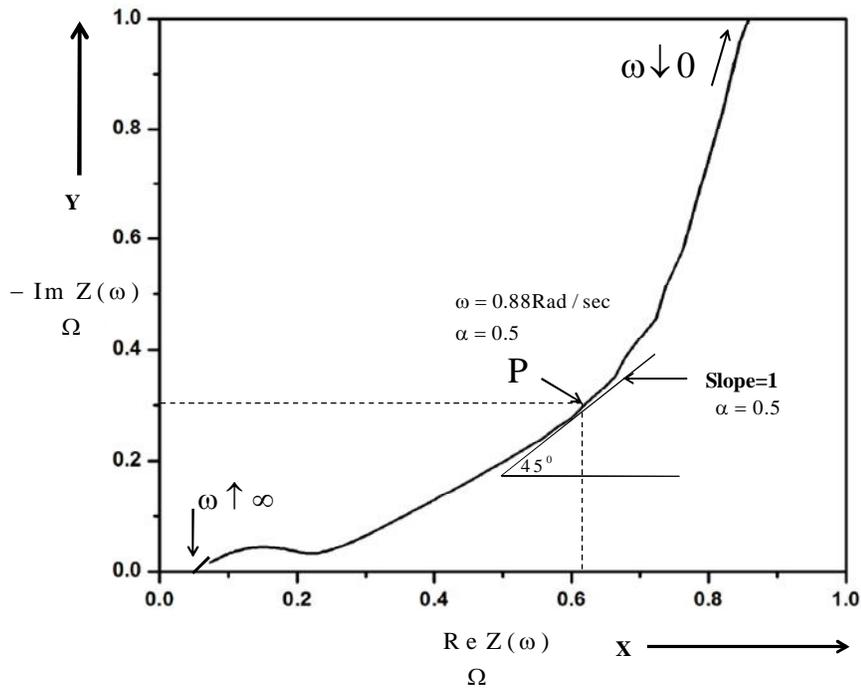


Figure-2: Nyquist's Diagram of Super-Capacitor C1

5. Charge Storage by step input voltage excitation to a fractional capacitor and ideal capacitor

Let at $t = 0$ $v(t) = V_m$ a step input of constant magnitude V_m is given to an uncharged capacitor with time varying capacity function as $c(t) = C_\alpha t^{-\alpha}$. Thus we have following from the expression $q(t) = c(t) * v(t)$

$$Q(s) = \mathcal{L}\{q(t)\} = \left(\mathcal{L}\{c(t)\}\right)\left(\mathcal{L}\{v(t)\}\right) = \left(\frac{C_\alpha \Gamma(1-\alpha)}{s^{1-\alpha}}\right)\left(\frac{V_m}{s}\right) = \frac{V_m C_\alpha \Gamma(1-\alpha)}{s^{2-\alpha}} \quad (26)$$

Doing inverse Laplace transform of above Eq. (26), we get the following

$$q(t) = \frac{V_m C_\alpha}{1-\alpha} t^{1-\alpha} = \frac{V_m C_{F-\alpha}}{\Gamma(2-\alpha)} t^{1-\alpha}, \quad C_{F-\alpha} = C_\alpha \Gamma(1-\alpha) \quad (27)$$

The current is

$$i(t) = \frac{dq(t)}{dt} = V_m C_\alpha t^{-\alpha} \quad (28)$$

This is Curie-von Schweidler relaxation law for dielectric stressed with constant voltage or Electric field [2]-[4], [6]-[8]. If the case we take for loss less ideal capacitor given by capacity function $c(t) = C_1 \delta(t)$, then $q(t) = c(t) * v(t)$, with $v(t) = V_m u(t)$, where $u(t)$ is unit step function at $t = 0$, is $q(t) = \mathcal{L}^{-1}\{C(s)V(s)\} = \mathcal{L}^{-1}\{C_1 V_m / s\} = C_1 V_m u(t)$. The current in this ideal case is $i(t) = \frac{dq(t)}{dt} = V_m C_1 \frac{du(t)}{dt} = V_m C_1 \delta(t)$. Both the cases are depicted in Figure-3; [1].

Capacity, charge, current for ideal capacitor vis-a-vis time varying capacitor to a step voltage excitation

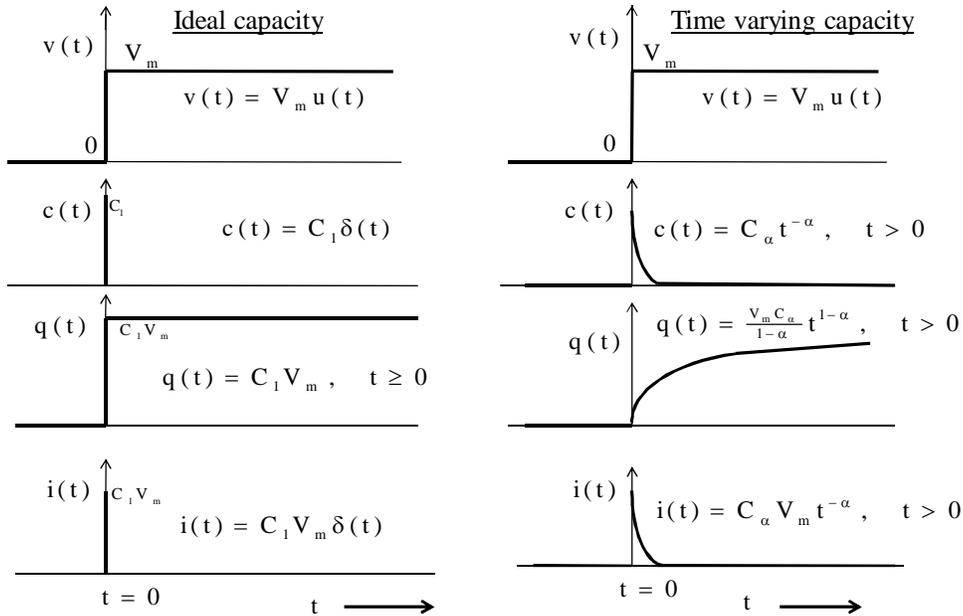


Figure-3: Charge in a ideal capacitor vis-à-vis time varying capacity function

We observe that when the step input $v(t)$ is kept 'ON' at V_m Volts for time T , $2T$ and $3T$ we get charge as $q(T) = \frac{V_m C_\alpha}{1-\alpha} T^{1-\alpha}$, $q(2T) = 2^{1-\alpha} \frac{V_m C_\alpha}{1-\alpha} T^{1-\alpha}$, $q(3T) = 3^{1-\alpha} \frac{V_m C_\alpha}{1-\alpha} T^{1-\alpha}$ respectively. In

limit $T \uparrow \infty$, we get $q(T)|_{T \uparrow \infty} = \infty$. This process leads to a new breakdown mechanism of capacitors noted in [1], [6], [7], called electrostatic breakdown of capacitors.

Figure-3 also says that $q(t)$ is instantaneously following $v(t)$ without any delay for ideal loss less capacitor case. This means that $q(t)$ does not have phase lag with $v(t)$ for ideal loss less capacitor case. Whereas for a fractional capacitor with capacity function $c(t) = C_\alpha t^{-\alpha}$ the charge function $q(t)$ is delayed w.r.t. $v(t)$ implying phase angle lag. This we had discussed earlier in Section-2 with sinusoidal analysis.

6. Memory effect in fractional capacitor

Thus we see if we keep afloat a capacitor not the ideal one, but a capacitor with capacity function $c(t) = C_\alpha t^{-\alpha}$, to a constant voltage V_m first for time T then $2T \dots$ the charge held will be more in second case, though the terminal voltage that we measure will be same as V_m . After holding for set time, we keep it open circuited for self discharging. Then in all the cases the self discharge decay of terminal voltage we will observe starting from V_m , with a different decay curves. This is because in second and third cases more charge needs to be drained out, in self-discharging case. Thus the capacitor is memorizing its time of charge, i.e. T . This is described in [6], [7], that is due to the formula $i(t) = C_{F-\alpha} D_t^\alpha v(t)$. This explanation is possible only with fractional capacitor and not with ideal capacitors, where we write $i(t) = C D_t^1 v(t)$.

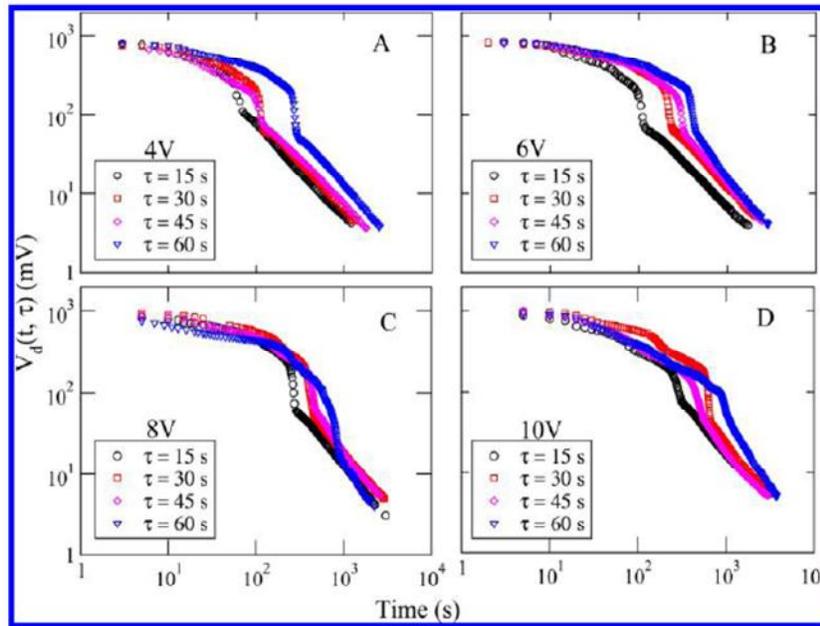


Figure-4: Memorizing charging time of applied electric-field in experiments with Laponite

The reasons of memory effect is due to porous nature of electrodes and due to non-Debye complex relaxation with distribution of several relaxing rates [8]-[10]. This non-Debye relaxation with several simultaneous relaxation gives constituent law as $i(t) = C_{F-\alpha} D_t^\alpha v(t)$ [8]-[10], where

the fractional derivative operator is non-local in nature mimicking the memorized dynamics, compared to $i(t) = C D_t^1 v(t)$, which is a local operator and point property having no memory. The details about charge storage in porous electrodes is explained in [1], by example of a pitcher holding water made with porous material.

The Figure-4 is experimental evidence that a relaxing system ; in this case, Laponite stressed with DC-Electric Field/ Voltage, has a memory of being connected to a voltage supply for during time τ and continues as if it is still connected to a non-zero voltage source, after the voltage source is switched-off. This Figure-4 is variation of self-discharge voltage $V_d(t, \tau)$ with time after the electric field is switched off at time $t = \tau$ for different applied voltages. The self-discharging curve is a function of DC-Electric field/Voltage holding time (τ). Therefore in a way the relaxing system is memorizing its history of charging time [14].

For ideal loss less (initially uncharged) capacitor with capacity function $c(t) = C_1 \delta(t)$, for $t \geq 0$, will hold charge as $q(t) = V_m C_1$, when put on a voltage $v(t) = V_m u(t)$; Figure-3. Therefore after any time $T, 2T \dots$ the charge will be same $q(T) = q(2T) = V_m C_1$, thereafter the self discharge decay curves in this case will not be differentiating depending amount of charging time T , the capacitor is placed on prior to self discharge. Thus there will be no-memory effect observed in case of ideal loss less capacitor, as observed in case of fractional capacitors; since amount of charge to be drained out in all cases is same.

7. Charge storage by ramp input voltage excitation to fractional capacitor and ideal capacitor

We apply a ramp voltage input to an uncharged capacitor- as $v(t) = (V_m / T)t$, i.e. applied at $t = 0$ and it linearly rises from zero volts to V_m volts, in time $t = T$. We have $V(s) = (V_m / Ts^2)$.

We apply $q(t) = c(t) * v(t)$; with $c(t) = C_\alpha t^{-\alpha}$, as time varying capacity function. To get the following charge function in Laplace domain

$$Q(s) = \left(\frac{C_\alpha \Gamma(1-\alpha)}{s^{1-\alpha}} \right) \left(\frac{V_m}{Ts^2} \right) = \frac{V_m C_\alpha \Gamma(1-\alpha)}{Ts^{1+(2-\alpha)}} = \frac{V_m C_{F-\alpha}}{s^{1+(2-\alpha)} T} \quad (29)$$

Doing inverse Laplace transform of Eq. (29) we obtain $q(t)$ as follows

$$\begin{aligned} q(t) &= \frac{V_m C_\alpha \Gamma(1-\alpha)}{T(\Gamma(3-\alpha))} t^{2-\alpha} = \frac{V_m C_\alpha}{T} \frac{1}{(1-\alpha)(2-\alpha)} t^{2-\alpha}, \quad \Gamma(m+1) = m\Gamma(m) \\ &= \frac{V_m}{T} \frac{C_{F-\alpha}}{\Gamma(3-\alpha)} t^{2-\alpha}, \quad 0 \leq t \leq T, \quad C_{F-\alpha} = C_\alpha \Gamma(1-\alpha) \end{aligned} \quad (30)$$

The current $i(t)$ is following, that we get by differentiation of Eq. (30)

$$i(t) = \frac{dq(t)}{dt} = \frac{V_m C_\alpha}{T(1-\alpha)} t^{1-\alpha}, \quad 0 \leq t \leq T \quad (31)$$

We get the charge at the end of time $t = T$ as

$$q(T) = \frac{V_m C_\alpha}{(1-\alpha)(2-\alpha)} T^{1-\alpha} \quad (32)$$

For ideal capacitor we have capacity function as $c(t) = C_1 \delta(t)$, we write charge as $q(t) = c(t) * v(t)$ as following

$$\begin{aligned} Q(s) &= (\mathcal{L}\{c(t)\})(\mathcal{L}\{v(t)\}) = (\mathcal{L}\{C_1 \delta(t)\})(\mathcal{L}\{(V_m / T)t\}) \\ &= (C_1) \left(\frac{V_m}{Ts^2} \right) = \frac{V_m C_1}{Ts^2} \end{aligned} \quad (33)$$

Taking inverse Laplace transform of Eq. (33) we write the following

$$q(t) = \frac{V_m C_1}{T} t, \quad t > 0 \quad (34)$$

We have from Eq. (34); at $t = T$, the stored charge as $q(T) = V_m C_1$. This is the same as the charge stored at any time $t \geq 0$, $q(t) = V_m C_1$ when $v(t) = V_m u(t)$ for step-input case, Figure-3. Thus an ideal loss-less capacitor charged to voltage V_m either via ramp input or via step input, will hold charge $V_m C_1$. This ideal capacitor when kept as open circuited for self discharge mode, will start discharging same amount of charge and the discharge curves will not have any difference in fall rates, as for both cases the discharge voltage will be starting from V_m . There will no memory effect observed for an ideal capacitor with ramp as well as step input charging to voltage V_m .

The current in the ideal capacitor for ramp input $v(t) = V_m t / T$ from Eq. (34) is as follows

$$i(t) = \frac{dq(t)}{dt} = \frac{V_m C_1}{T} \quad (35)$$

This we verify from ideal capacitor equation that is following

$$i(t) = C_1 \frac{dv(t)}{dt} = C_1 \frac{d}{dt} (V_m t / T) = \frac{V_m C_1}{T} \quad (36)$$

The charge function obtaining therefore from Eq. (36) is as follows

$$q(t) = \int_0^t i(\tau) d\tau = \int_0^t \left(\frac{V_m C_1}{T} \right) d\tau = \frac{V_m C_1}{T} t \quad (37)$$

The above derivational steps Eq. (33) to Eq. (37) for ideal-loss-less capacitor is verification and justifies that we apply $c(t) = C_\alpha t^{-\alpha}$ as we did for step input case in previous section when voltage is changed at $t = 0$, (in ramp case too), for a fractional capacitor. This comes from the above observations Eq. (33) to Eq. (37) that for ideal loss less capacitor case, the capacity function i.e. $c(t) = C_1 \delta(t)$ gets applied at $t = 0$ (for ramp case too).

8. Comparison of charge storage by step and ramp input excitation & capacitor memorizing the shape of input excitation

For the step input with voltage, held for time $t = T$ we have the charge as $q(T) = \frac{V_m C_\alpha}{1-\alpha} T^{1-\alpha}$, and we have charge at the end of $t = T$ for a ramp input as $q(T) = \frac{V_m C_\alpha}{(1-\alpha)(2-\alpha)} T^{1-\alpha}$. We write the ratio as follows

$$\frac{q(T)|_{\text{STEP}}}{q(T)|_{\text{RAMP}}} = \frac{\frac{V_m C_\alpha}{1-\alpha} T^{1-\alpha}}{\frac{V_m C_\alpha}{(1-\alpha)(2-\alpha)} T^{1-\alpha}} = 2 - \alpha \quad (38)$$

We observe that if we hold the voltage V_m Volts for time T and charge a capacitor, then we will be holding $(2 - \alpha)$ times the charge if we ramp the voltage at rate V_m / T from zero to V_m Volts, in time T . Now after this process if we keep the capacitors for self discharging mode, for both the cases the voltage decay will start from V_m . For step-charging case, since amount of charge held is more, it will take longer time to self discharge as compared to case with ramp-charging. This we expect from the memory effect.

Therefore we can say here the capacitor has memorized the shape of its excitation input. This we again got from using the formula $q(t) = c(t) * v(t)$. The comparison between step input voltage charging and ramp input voltage charging is depicted in Figure-5. This study on similar lines about memory effect from step and ramp charging is also shown in [15]; but here we have used the new formula $q(t) = c(t) * v(t)$.

This ramp and step voltage excitation differentiation will not be observed in self-discharge curves, for an ideal loss less capacitor with capacity function as $c(t) = C_1 \delta(t)$, when charged to voltage V_m , since in both the cases same amount of charge i.e. $V_m C_1$ needs be drained out. This we have described in previous section. Thus an ideal capacitor will not be memorizing the shape of its charging profile $v(t)$; whereas fractional capacitor memorizes the charging profile.

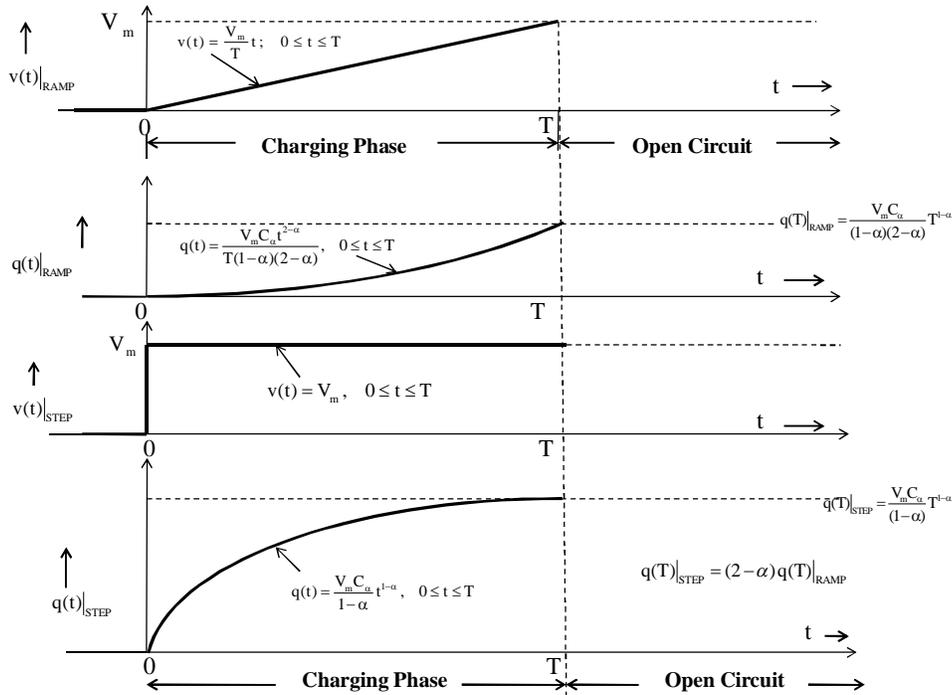


Figure-5: Step input voltage charging and Ramp input voltage charging

9. Discussions

We have compared the step input and ramp input excitation, by considering while we apply the excitation voltage, the response a capacitor produces to charge itself is by same time varying capacity function, i.e. $c(t) = C_\alpha t^{-\alpha}; 0 < \alpha < 1$, for a fractional capacitor. In actual cases the two input functions are having frequency components ω from 0 to ∞ (i.e. neglecting truncation of

the inputs at time $t = T$). As demonstrated while discussing Nyquist's diagrams we will be having different values at different frequencies for α and $C_{F-\alpha}$. Therefore; we may ask how far this assumption is valid. We do **the** qualitative analysis for this assumption.

Unit steps function **u(t)** defined as $u(t) = 1; t \geq 0$ and $u(t) = 0; t < 0$ (without truncation) has Fourier transform as $\mathcal{F}\{u(t)\} = \frac{1}{2}\left(\delta(\omega) - \frac{j}{\omega}\right)$. A unit ramp $r(t)$ described as $r(t) = t; t \geq 0$ and $r(t) = 0; t < 0$ (without truncation) is having Fourier transform as $\mathcal{F}\{r(t)\} = -\frac{1}{\omega^2} + j\frac{d\delta(\omega)}{d\omega}$. We observe both $\mathcal{F}\{u(t)\}$ and $\mathcal{F}\{r(t)\}$ have DC component and frequency components amplitude varying as ω^{-1} and ω^{-2} respectively-but loaded highly towards DC i.e. low frequency. Therefore even if there is difference in α and $C_{F-\alpha}$, that will be small. Moreover these Fourier components of unit step and unit ramp function will be modified by a Fourier transform of 'Rectangular Window function' centered at time $T/2$, of height unity. Thus one may be justified in selecting same α and C_α for the capacity function $c(t)$ acting for step as well as ramp input, to compare the charge storage function. This analysis is done in [15] shows the parameters for ramp and step excitations are not widely varying.

The concept of charge storage as applied here by taking convolution operation i.e. $q(t) = c(t) * v(t)$ instead of usual formula $q(t) = c(t)v(t)$ is very important in dielectric relaxation studies where the capacitor formed as classical electronics capacitor is also having Curie-von Schweidler current relaxation law experimentally verified, as reported in [6], and thus fractional capacitor is reality. With use of this formula we have inferred various phenomena of fractional capacitor and ideal loss less capacitor. We have seen applying this formula $q(t) = c(t) * v(t)$ we get current of fractional capacitor leading by $\alpha\pi/2$ to **the** voltage input, and charge function $q(t)$ lags by **an** angle $\phi = (1 - \alpha)\pi/2$ to a voltage input. From here we also proposed an idea of re-defining loss tangent as $\tan \phi$ for a fractional capacitor case, where ϕ is lag angle of $q(t)$ w.r.t. $v(t)$ in sinusoidal analysis. Using this formula we have discussed the memory effect that is found for fractional capacitors, and showed that not only the fractional capacitor memorizes its float voltage time T for step-input voltage, but also memorizes the shape of excitation i.e. step excitation or ramp excitation while T remains same. The phenomena of fractional capacitor are more prominent in super capacitor studies, as reported in [15]-[22], [37]-[38]. Therefore in this view the concept of charge storage formula is revisited, for further usage in dielectric studied and super-capacitor studies. Just recently experimental validation is carried out on this new formula [40], with comparison with other non-linear numerical simulations for capacitors and super-capacitors.

The formula $q(t) = c(t) * v(t)$ can be verified for several other types of excitation wave forms for $v(t)$ like, square wave, triangular wave, also for RC circuit and LC with fractional capacitors. That we are not reporting in this paper.

10. Conclusions

We have applied the new formula of charge storage i.e. via convolution operation, of time varying capacity function and voltage stress for a fractional capacitor. This new formulation is different to the earlier used formula of multiplication of capacity and voltage function. We have discussed various results obtained for different excitation voltages- sinusoidal, step and ramp; and

also revisited the impedance formula, and Nyquist's diagrams and the concept of loss-tangent and memory in fractional capacitors. We have given interpretations of the various theoretical results that were obtained by this new formulation, thus verified the usage of this new expression. We have not yet applied this to practical cases in our project as this theoretical development very new, but plan to have further experimental and theoretical studies on this new formula, like application in estimation state of charge (SOC) in supercapacitors charge discharge applications, parameter extraction by Hysteresis plot where use this formula for supercapacitors, the insight into new way of defining loss-tangent as we obtained from this formula, and applications to several dielectric relaxation experiments where memory is observed.

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