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On a possible physical origin of the constant phase element

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ABSTRACT

Despite the numerous use of the constant phase element (CPE) in the modeling of the impedance characteristics of the electrochemical systems, the physical reasoning of this non-intuitive element is not clear. In this paper, the CPE impedance is analytically calculated using the anomalous diffusion theory. The fractional calculus and the anomalous diffusion are first reviewed. It is shown that the chance inequality in the random walk in a porous media can result in an anomalous diffusion. Then, the Boltzmann distribution of the particles used in the Gouy-Chapman theory of the double layer is modified to determine the double layer capacitance. Finally, the impedance of the double layer is calculated which is equivalent to the CPE impedance reported in literature. It is shown that this novel theory covers the interpretations previously presented for the CPE and its relation to the fractal dimension and the pore size distribution of the porous media.

1. Introduction

The Nyquist plots resulted from the impedance measurements of different electrochemical systems such as biological membranes [1], muscles [2] and a solid and porous electrode/electrolyte interface [3–5] reveal an impedance plot which cannot be obtained by a combination of ordinary electrical elements (e.g., resistances and capacitances). While the parallel connection of a capacitor and a resistor results in a semi-circle in the Nyquist plot which is symmetric around abscissa (i.e., the center of the semi-circle is on the x-axis), the measured Nyquist plots consist of depressed semi-circle whose center is below the x-axis. These curves can be produced by a parallel combination of an ordinary resistance and a non-intuitive element called 'constant phase element' (CPE) which has the impedance in the form of

$$Z_{\mathrm{CPE}} = \frac{1}{Q(j\omega)^{\alpha}} \tag{1}$$

where ω is angular frequency and $j = \sqrt{-1}$. Here, α is a non-dimensional number called the CPE power and $0 < \alpha < 1$. Clearly, the CPE becomes an ordinary capacitance if $\alpha = 1$. Also, the CPE impedance becomes independent of the frequency and CPE responds as a plain resistance if $\alpha = 0$. Also, $\alpha = 1/2$ and $\alpha = -1$ result in Warburg and inductive elements, respectively. The farther the α parameter from unity, the more depressed the resultant semi-circle in the Nyquist plot. The Q parameter in Eq. (1) is referred to as the magnitude of the CPE. Unlike the plain capacitor (which has the unit of Farad (F)), the parameter Q in Eq. (1) has the unit of $\mathrm{Fs}^{\alpha-1}$, where s stands for seconds.

There is no consensus about the physics behind the CPE in literature [3]. The CPE power (α) has been reported to be a function of the surface roughness [6], fractal dimension [7,8] or the pore size distribution [9] of the porous electrode. However, it has mostly assumed to be related to different time constants of the processes occurring in the porous electrode [e.g.,10–18]. The Voigt model (representing an equivalent circuit consisting of a series of blocks of resistors and capacitors that are connected in parallel) is normally used as a measurement model to study the CPEs [e.g.,12,13]. While the Voigt model is an effective tool, it cannot represent the fundamentals of the origin of the CPEs. This can be explained as follows: the Voigt model can be well fitted (with any desired accuracy) to the CPE curve (in the Nyquist plot) by adding enough elements (e.g., resistors and capacitors) to the model. Each combined resistor and capacitor block in the Voigt model can be interpreted as a phenomenon with a specific time constant. However, this does not mean that the CPE is originally the result of these phenomena and time constants. In other words, the Voigt model can only present the CPE mathematically, but not physically. It is necessary to mention that any impedance measurement which results in a curve in the Nyquist plot can theoretically be fitted using the Voigt model [19].

In this paper, the physics behind the origin of the CPE is presented using the anomalous diffusion concept [20]. As a result,

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the well-known impedance relation of the CPE (Eq. (1)) is derived. It is shown that this new approach is a comprehensive framework covering all the previously mentioned interpretations [6–9] of the physics of the CPE. To obtain the CPE impedance relation, the double-layer theory is needed to be reconsidered using the anomalous diffusion theory which itself needs the fractional calculus introduction. As this framework is not normally discussed in the CPE literature, the fractional derivative concept is first briefly introduced. The anomalous diffusion and the random walk theory are then briefly reviewed. The Gouy-Chapman theory of the double-layer concept is then revisited using the anomalous diffusion concept. Finally, the CPE impedance is calculated. More specifically, the CPE power (α) is shown to be equal to the anomalous diffusion power (n).

2. Fractional derivative

The Fourier transform of the n^{th}-order derivative of a function $f(t)$ is written as

$$\Im\left\{\frac{d^n f(t)}{dt^n}\right\} = (j\omega)^n F(\omega) \tag{2}$$

where $\Im\{f(t)\} = F(\omega)$ is the Fourier transform. While n is normally considered as a natural number, relations similar to Eq. (2) can be introduced to define n^{th}-order derivative for real numbers (also referred to as fractional derivative). In fact, this concept (first presented by Leibniz in 1695 [20]) is older than Fourier transform itself, as old as the normal derivation concept. The Riemann-Liouville version of the n^{th}-order fractional derivative of a function $f(t)$ is defined as [e.g.,20]

$$D_t^n f(t) = \frac{1}{\Gamma(p-n)}\frac{d^p}{dt^p}\int_0^t \frac{f(x)}{(t-x)^{1-p+n}}dx \tag{3}$$

where p is an integer number such that $p-1 < \mathrm{Re}(n) \le p$ and Γ denotes the gamma function. For $0 < n < 1$, this operator can be simplified as

$$D_t^n f(t) = \frac{1}{\Gamma(1-n)}\frac{d}{dt}\int_0^t \frac{f(x)}{(t-x)^n}dx \tag{4}$$

As an example, the fractional derivative of a power function can be determined as [21]

$$D_t^n t^k = \frac{\Gamma(k+1)}{\Gamma(k+1-n)}t^{k-n} \tag{5}$$

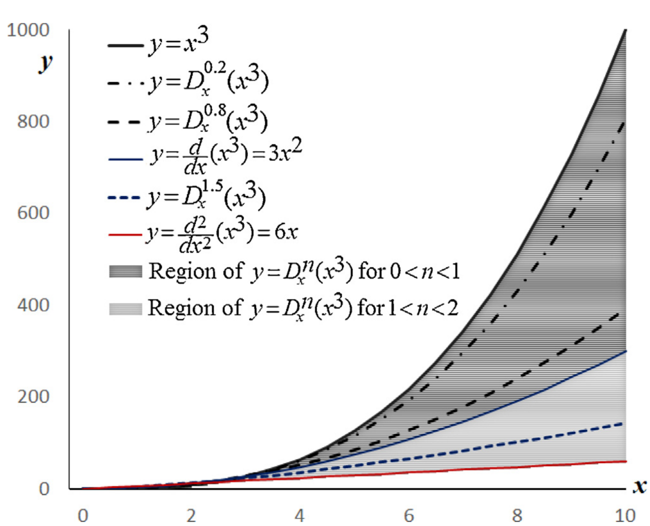

Fig. 1. The natural and fractional derivatives of the example function $y = x^3$.

which is in agreement with the normal derivative definition when n is a natural number. Fig. 1 shows different natural and fractional derivatives of a sample function ($y = x^3$). While the first (and second) derivative operators are normally considered as basic tools to calculate the slope (and curvature) of a function, those can also be interpreted as *discrete* operators which convert a function to another function, and the latter function is called the derivative of the former one. Roughly speaking, this concept of fractional derivative is used to convert this *discrete* operator to a *continuous* one. As an example, Fig. 1 depicts that all the functions resulted from n^{th}-order fractional derivation of the function $y = x^3$ will lie between the $y = x^3$ and $y = \frac{d}{dx}(x^3) = 3x^2$ curves for $0 < n < 1$ for positive x values.

Finally, the following two properties of the Riemann-Liouville fractional derivative are specifically needed to be mentioned here [21]

$$D_t^n 1 = \frac{1}{\Gamma(1-n)}t^{-n} \tag{6}$$

$$D_t^n t^{n-1} \equiv 0 \tag{7}$$

3. Anomalous diffusion and random walk theory

Random walk theory is in fact a framework which relates the Brownian motion to the diffusion equation. The random walk theory describes the transport rate of a particle which moves completely randomly in each time step (see Ref. [20] for the history of the theory). Using this theory, the mean square displacement of a particle at a time t can be estimated to be [22]

$$\left\langle x^2(t)\right\rangle = 2\Lambda t \tag{8}$$

where Λ is the diffusion coefficient. This linear dependence of the mean square displacement to the time is a characteristic of the Brownian motion [20]. However, the physical systems do not always obey the above-mentioned relation; thus, the mean square displacement has to be generalized in the following form:

$$\left\langle x^2(t)\right\rangle \sim t^n \tag{9}$$

This model of transport is called anomalous diffusion. Specifically, it is called subdiffusion if $0 < n < 1$ (slower than normal diffusion) and superdiffusion if $n > 1$ (faster than normal diffusion). There is an extensive range of physical systems which show subdiffusive and superdiffusive characteristics [20]. For instance, the charge transfer in semiconductors and transport in fractal structures and porous media show subdiffusive characteristics. On the other hand, turbulent diffusion, bacterial motion and quantum optics are just examples of superdiffusion transport. For the reasons which will be clear hereafter, the subdiffusion process is in special interest here.

In addition to Eq. (9), other interpretations have also been presented for the subdiffusion power n. In a fractal dimension, the power n can be shown to be [23,24]

$$n = \frac{d_s}{d_f}$$

which d_s and d_f are spectral (fracton) and fractal dimensions of the structure, respectively [24]. Using the continuous time random walk theory, another interpretation of n can be obtained. The continuous time random walk theory is in fact the extension of the random walk theory in which the length of the jumps of the particle and also the waiting time between each jump is obtained