FRACTAL CALCULUS FOR MODELING ELECTROCHEMICAL CAPACITORS UNDER DYNAMICAL CYCLING

by

Xian-Yong LIU [a], ***Yan-Ping LIU*** [b*], ***and Zeng-Wen WU*** [a]

[a] Robotics Institute, Ningbo University of Technology, Ningbo, Zhejiang Province, China
[b] College of Ocean Science and Technology, Zhejiang Ocean University, Zhoushan, Zhejiang Province, China

Original scientific paper
https://doi.org/10.2298/TSCI200308028L

The differential model for electrochemical capacitors under dynamical cycling results in discontinuity of the electric current. This paradox makes theoretical analysis of the electrochemical capacitors much difficult, and there is not universal approach to treatment of the problem. This paper finds that the fractal calculus can be powerfully applied to the problem, and a continuous electric current can be obtained as it should be.

Key words: *fractal derivative, fractional calculus, periodic solution, discontinuity*

Introduction

Due to rapid development of nanotechnology, electrochemical capacitors have been caught much attention due to their enhanced properties [1-7], inorganic-nanocarbon hybrid materials [2], nanostructured materials [3], graphene [4], nanoscale porous fibers [8-15], can be used for ultracapacitors. It is of great importance to have a fast look into the current-voltage relationship under various dynamical cycling, especially dynamical cycling with discontinuous or unsmooth function of period as illustrated in fig. 1.

We consider a capacitor and a resistor in parallel in an electrochemical system, the current can be expressed [1]:

$$i(t) = \frac{V(t)}{R} + C\frac{\mathrm{d}V}{\mathrm{d}t} \tag{1}$$

where V is the electromotive force which is a saw-tooth function as illustrated in fig. 1, i – the electric current, C – the capacitance, and R – the resistance.

Though the applied voltage is unsmooth, the current in the circuit *vs.* the external voltage should be a continuous curve, however, eq. (1) produces discontinuity points respect to the inversion points of the external voltage, the electric current presents a discontinuity at $t = 0$ and $t = T/4$, respectively, [1]:

$$\Delta i(0) = \frac{4V_0C}{T} \tag{2}$$

$$\Delta i\left(\frac{T}{4}\right) = \frac{8V_0C}{T} \tag{3}$$

so the model given in eq. (1) has to be modified.

* Corresponding author, e-mail: liuyp@zjou.edu.cn

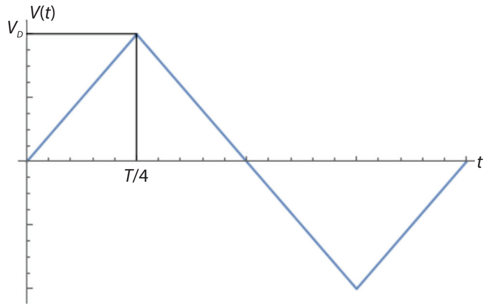

Figure 1. Dynamical cycling with a saw tooth function of period *T*

Fractal calculus for the supercapacitor

Due to porous structure of the electrodes, a fractional model was suggested to describe electrochemical supercapacitors/ultracapacitors [16, 17], and the continuum model given in eq. (1) should be avoided. In this paper, we modify eq. (1):

$$i(t)=\frac{V(t)}{R}+C\frac{\mathrm{d}V}{\mathrm{d}t^{\alpha}} \tag{4}$$

where $\mathrm{d}V/\mathrm{d}t^{\alpha}$ is a fractal derivative defined [16, 17]:

$$\frac{\mathrm{d}V}{\mathrm{d}t^{\alpha}}(t)=\Gamma(1+\alpha)\lim_{\Delta t=t^{+}-t^{-}\to\Delta t_0}\frac{V(t^{+})-V(t^{-})}{(t^{+}-t^{-})^{\alpha}} \tag{5}$$

where α is the fractal order, Δt_0 – the lowest hierarchical time, $\Delta t_0 \neq 0$, beyond which all functions are assumed to be continuous. When $t = 0$ and $T/4$, the fractal derivatives can be defined, respectively:

$$\frac{\mathrm{d}V}{\mathrm{d}t^{\alpha}}(0)=\Gamma(1+\alpha)\lim_{\Delta t=0^{+}-0^{-}\to\Delta t_0}\frac{V(0^{+})-V(0^{-})}{(0^{+}-0^{-})^{\alpha}}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t^{\alpha}}\left(\frac{T}{4}\right)=\Gamma(1+\alpha)\lim_{\Delta t=0^{+}-0^{-}\to\Delta t_0}\frac{V\left[\left(\frac{T}{4}\right)^{+}\right]-V\left[\left(\frac{T}{4}\right)^{-}\right]}{\left[\left(\frac{T}{4}\right)^{+}-\left(\frac{T}{4}\right)^{-}\right]^{\alpha}}$$

Using a transform [17-21]:

$$s=pt^{\alpha} \tag{6}$$

where p is a constant, eq. (4) becomes:

$$i(s)=\frac{V(s)}{R}+pC\frac{\mathrm{d}V}{\mathrm{d}s} \tag{7}$$

Solving eq. (7) we have:

$$i_1(s)=\frac{4V_0 s}{RT}+\frac{4pV_0C}{T},\quad 0\le t\le\frac{T}{4} \tag{8}$$

$$i_2(s)=\left(\frac{2V_0}{R}-\frac{4V_0 s}{RT}\right)-\frac{4pV_0C}{T},\quad \frac{T}{4}\le t\le\frac{3T}{4} \tag{9}$$

$$i_3(s)=\left(\frac{-4V_0}{R}+\frac{4V_0 s}{RT}\right)+\frac{4pV_0C}{T},\quad \frac{3T}{4}\le t\le T \tag{10}$$

In view of eq. (6), we have:

$$i_1(t)=\frac{4pV_0t^{\alpha}}{RT}+\frac{4pV_0C}{T},\quad 0\le t\le\frac{T}{4} \tag{11}$$

$$i_2(t)=\left(\frac{2V_0}{R}-\frac{4pV_0t^{\alpha}}{RT}\right)-\frac{4pV_0C}{T},\quad \frac{T}{4}\le t\le\frac{3T}{4} \tag{12}$$

$$i_3(t)=\left(\frac{-4V_0}{R}+\frac{4pV_0t^\alpha}{RT}\right)+\frac{4pV_0C}{T},\ \frac{3T}{4}\le t\le T \tag{13}$$

The continuity of the electronic current requires:

$$i_1(0)=i_3(T) \tag{14}$$

$$i_1\left(\frac{T}{4}\right)=i_2\left(\frac{T}{4}\right) \tag{15}$$

or

$$\frac{4pV_0C}{T}=\left(\frac{-4V_0}{R}+\frac{4pV_0T^\alpha}{RT}\right)+\frac{4pV_0C}{T} \tag{16}$$

$$\frac{4pV_0}{RT}\left(\frac{T}{4}\right)^\alpha+\frac{4pV_0C}{T}=\left(\frac{2V_0}{R}-\frac{4pV_0}{RT}\right)\left(\frac{T}{4}\right)^\alpha-\frac{4pV_0C}{T} \tag{17}$$

Simplifying eqs. (16) and (17):

$$pT^{\alpha-1}=1 \tag{18}$$

$$\frac{8pV_0C}{T}=\left(\frac{2V_0}{R}-\frac{8pV_0}{RT}\right)\left(\frac{T}{4}\right)^\alpha \tag{19}$$

For given V_0, R, C, and T, we can easily determine α and p. We can also apply the homotopy perturbation method [22-28] to approximately solve α and p from eqs. (18) and (19).

Conclusion

In this short paper, we suggest a modification of resistor-capacitor circuit model for electrochemical capacitors using fractal calculus. The paradox for discontinuous currents arising in a continuum model given in eq. (1) can be completely eliminated, making the modification suitable for modeling supercapacitors/ultracapacitors.

Acknowledgment

This work has been financially supported by the Public Projects of Zhejiang Province (LGG18F030013) and Research start-up fund of Ningbo University of Technology.

References

[1] Zaccagnini, P., *et al*., Modelling of Electrochemical Capacitors under Dynamical Cycling, *Electrochimica Acta*, 296 (2019), Feb., pp. 709-718
[2] Wang, H., Dai, H., Strongly Coupled Inorganic-Nanocarbon Hybrid Materials for Energy Storage, *Chem. Soc. Rev*., *42* (2013), 7, pp. 3088-3113
[3] Arico, A. S., *et al.*, Nanostructured Materials for Advanced Energy Conversion and Storage Devices, *Nature Material*s, *4* (2005), 5, pp. 366-377
[4] Stoller, M. D., *et al*., Graphene-Based Ultracapacitors, *NanoLetters*, *8* (2008), 10, pp. 3498-3502
[5] Li, X., *et al*., Stable RuO_2-Based Ternary Composite Electrode of Sandwiched Framework for Electrochemicalcapacitors, *Electrochimica Acta*, *289* (2018), Nov., pp. 292-310
[6] Priyadharsini, N., *et al*., Morphology-Dependent Electrochemical Properties of Sol-Gel Synthesized $LiCoPO_4$ for Aqueous Hybrid Capacitors, *Electrochimica Acta*, *289* (2018), Nov., pp. 516-526
[7] Li, R. B., *et al*., Facile Synthesis of Hierarchical Mesoporous Beta-Manganese Dioxide Nanoflowers with Extremely High Specific Surface Areas for High-Performance Electrochemical Capacitors, *Electrochimica Acta*, *284* (2018), Sept., pp. 52-59

[8] Peng, N. B., *et al*., A Rachford-Rice Like Equation for Solvent Evaporation in the Bubble Electrospinning, *Thermal Science*, *22* (2018), 4, pp. 1679-1683
[9] Tian, D., He, J.-H., Macromolecular Electrospinning: Basic Concept and Preliminary Experiment, *Results in Physics*, *11* (2018), Dec., pp. 740-742
[10] Yin, J., *et al*., Numerical Approach to High-Throughput of Nanofibers by a Modified Bubble-Electrospinning, *Thermal Science*, *24* (2020), 4, pp. 2367-2375
[11] Ahmed, A. and Xu, L. Numerical analysis of the electrospinning process for fabrication of composite fibers, *Thermal Science*, *24* (2020), 4, pp.2377-2383
[12] Li, X. X., *et al*., Nanofibers Membrane for Detecting Heavy Metal Ions, *Thermal Science*, *24* (2020), 4, pp. 2463-2468
[13] Li, X. X., *et al*., The Effect of Sonic Vibration on Electrospun Fiber Mats, *Journal of Low Frequency Noise Vibration and Active Control*, *38* (2019), 3-4, pp. 1246-1251
[14] Wu, Y. K., and Liu, Y., Fractal-Like Multiple Jets in Electrospinning Process, *Thermal Science*, *24* (2020), 4, pp. 2499-2505
[15] He, J. H., Advances in Bubble Electrospinning, *Recent Patents on Nanotechnology*, *13* (2019), 3, pp. 162 -163
[16] He, J. H., Ain, Q. T., New Promises and Future Challenges of Fractal Calculus: From Two-Scale Thermodynamics to Fractal Variational Principle, *Thermal Scienc*e, *24* (2020), 2A, pp. 659-681
[17] He, J. H., Fractal Calculus and Its Geometrical Explanation, *Results in Physics*, *10* (2018), Sept., pp. 272-276
[18] Li, X.-X., *et al*., A Fractal Modification of the Surface Coverage Model for an Electrochemical Arsenic Sensor, *Electrochimica Acta*, *296* (2019), Feb., pp. 491-493
[19] Wang, Q. L., *et al*., Fractal Calculus and Its Application Explanation of Biomechanism of Polar Bear Hairs, *Fractals*, *26* (2018), 6, 1850086
[20] He, J. H., A Short Review on Analytical Methods for to a Fully Fourth Order Non-Linear Integral Boundary Value Problem with Fractal Derivatives, *International Journal of Numerical Methods for Heat and* Fluid-Flow, *30* (2020), 11, pp. 4933-4943
[21] Shen, Y., He, J.H., Variational Principle for a Generalized KdV Equation in a Fractal Space, *Fractals*, *28* (2020). 04, 2050069
[22] Wu, Y., He, J. H., Homotopy Perturbation Method for Non-Linear Oscillators with Co-Ordinate Dependent Mass, *Results in Physics*, *10* (2018), Sept., pp. 270-271
[23] He, J. H., Homotopy Perturbation Method with an Auxiliary Term, *Abstract and Applied Analysis*, *2012* (2012), ID857612
[24] He, J. H., Homotopy Perturbation Method with Two Expanding Parameters, *Indian Journal of Physics*, *88* (2014), 2, pp. 193-196
[25] Liu, Z. J., *et al*., Hybridization of Homotopy Perturbation Method and Laplace Transformation for the Partial Differential Equations, *Thermal Science*, *21* (2017), 4, pp. 1843-1846
[26] Li, X. X., He, C. H., Homotopy Perturbation Method Coupled with the Enhanced Perturbation Method, Journal of Low Frequency Noise, *Vibration and Active Control*, *38* (2019), 3-4, pp. 1399-1403
[27] He, J. H., Some Asymptotic Methods for Strongly Non-Linear Equations, *Int. J. Mod. Phys. B*, *13* (2006), 20, pp. 1141-1199
[28] Yu, D. N., *et al*., Homotopy Perturbation Method with an Auxiliary Parameter for Non-Linear Oscillators, *Journal of Low Frequency Noise*, *Vibration and Active Control*, *38* (2019), 3-4, pp. 1540-1554

Paper submitted: March 8, 2020
Paper revised: June 15, 2020
Paper accepted: June 15, 2020