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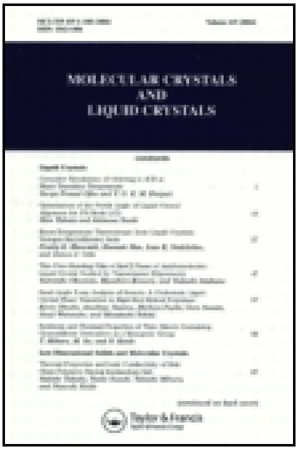

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Fractal Immtttance of Molecular Assemblies-A Prospect of Its Applications-

M. Sugi [a], Y. Hirano [a], H. Chiba [a], J. Kawata [a] & K. Saito [a b]

[a] Toin University of Yokohama, Aoba-ku, Yokohama, 225, JAPAN

[b] Electorotechnical Laboratory, Tsukuba-shi, Ibaraki, 305, JAPAN

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FRACTAL IMMITTANCE OF MOLECULAR ASSEMBLIES -A PROSPECT OF ITS APPLICATIONS-

M. SUGI, Y. HIRANO, H. CHIBA, J. KAWATA and K. SAITO*
Toin University of Yokohama, Aoba-ku, Yokohama 225, JAPAN
*Electorotechnical Laboratory, Tsukuba-shi, Ibaraki 305, JAPAN

Abstract A summary is given of a novel category of circuit elements based on the power-law conductivity (PLC) found in various organic and inorganic materials. This category, the fractal immittance device (FD), acts as a non-integer-rank differential/integral operator associated with a kind of memory effects. The guidelines for its hardware realization in the form of thin film devices utilizing the organized molecular assemblies are presented together with the fundamentals of it.

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INTRODUCTION

Since the early 1980's, a variety of ideas have been proposed aiming at the utilization of organic molecules in electronics, referring to the advances in the research on organic materials and life science.[1] Although it was worth envisaging ambitious goals, measures must have first been taken to bridge the chasm between electronics and materials science. In any realistic case, the output of molecular electronic devices may be further processed using CPU's which are still vigorously developing along the line of silicon technology. These considerations lead to the following items.[2]

(1) The prototype of device functions should be sought after in the physico-chemical properties of stable systems,

(2) The devices to be realized should have prospects beyond the substitutes of conventional ones in the present-day electronics, and,

(3) The device concept and the theory of networks should be expressed in the same mathematical terms as used in the conventional electronics.

We have recently shown that the power-law conductivity (PLC), $\sigma(\omega) \propto \omega^a$ with $0<a<1$ in the frequency domain,[3] satisfies the above items for a candidate of device prototype, and that a novel category, the power-law-case or fractal-immittance device (FD), can be realized.[2,4-8]

In the present paper, a summary is given of the guidelines for hardware realization of FD in the form of thin film devices utilizing the PLC behavior of organized molecular assemblies together with the fundamentals of FD.

LIMIT OF THE CONVENTIONAL ELECTRONIC CIRCUITS

The admittances of a resistor R, a capacitor C and an inductor L are expressed as s^0R^{-1}, sC and $s^{-1}L$, respectively, using the complex angular frequency s. Here, s and s^{-1} correspond to the differential and the integral actions in the time domain, respectively. The operational actions remain conserved in the circuits, each associated with a set of differential/integral equations. This is nothing other than the basis of analogue computers flourished some tens of years ago.

The irrational powers of s, however, never appear in the associated equations if the circuit is composed of finite numbers of R, C and L. The conventional analogue computation is therefore limited to the integer-rank equations, and a novel category of circuit elements is required for dealing with the non-integer-rank problems.

POWER-LAW CONDUCTIVITY

The power-law conductivity (PLC) in the s-domain is written as

$$\sigma(s) = \sigma_F(a)s^a \tag{1}$$

where $\sigma_F(a)$ is a positive coefficient. According to the theory of operational calculus, Eq.(1) indicates that PLC corresponds to a non-integer-rank differential $\sigma_F(a)d^a/dt^a$. The PLC behavior, often ascribed to the fractal distribution of relaxation times, is associated with the anomalous aftereffect referred to as the long-time tail, which is represented by a current response to a step voltage as

$$i(t) = \frac{\sigma_F(a)}{\Gamma(1-a)}t^{-a} \tag{2}$$

as shown in Fig. 1.[2]

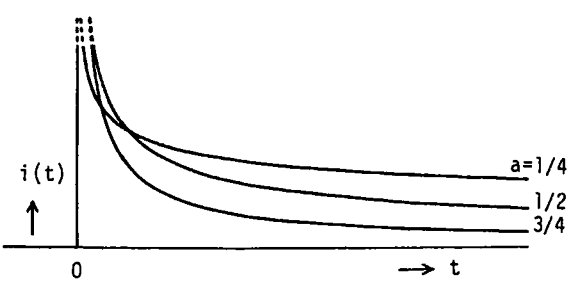

FIGURE1 Long-time-tail behavior of power-law conductivity (PLC). Transient current response $i(t)$ of PLC admittance to a unit step voltage is plotted against time t for the varying value of exponent a.

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PLC has been found in a variety of organic and inorganic systems. The following is a brief list according to A. K. Jonscher:[3]

(1) Conventional low-loss dielectrics such as SiO_2 and polyethylene terephthalate,

(2) Typical dipolar materials such as supercooled electrolyte solutions and ionic glasses,

(3) Hopping electronic systems such as crystalline Si in the impurity conduction range, chalcogenide glasses, and organic thin films prepared using LB, vacuum evaporation, casting and other techniques,

(4) Ionic conductors such as ruby mica and other layered compounds,

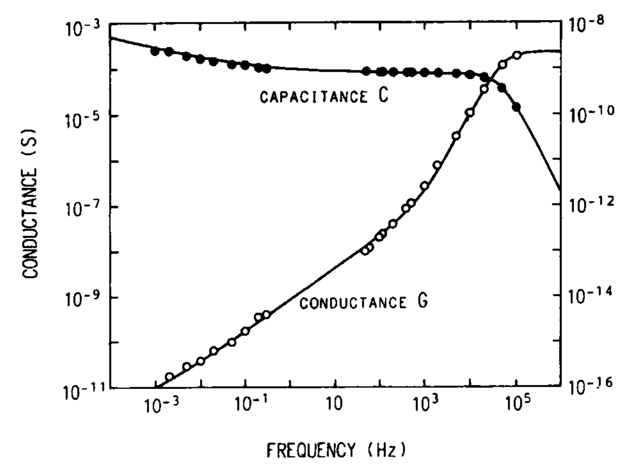
(5) Non-ideal p-n junctions with a high density of interface states or mobile ions,

(6) Humid materials such as zeolites and cellulose under humid conditions,

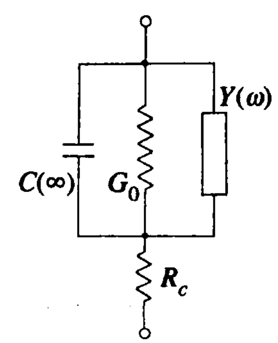
(7) Electrode-electrolyte interfaces with fractal geometries, and,

(8) Biological materials such as suspension of cells in aqueous solutions and animal tissues.

(a)



(b)



(c)

FIGURE 2 PLC behavior observed for an Al / mixed monolayer / Al junction. A merocyanine (DS) and a fatty acid (C_{20}) shown in (a) are mixed with [DS]:[C_{20}]=1:2. The conductance G and capacitance C are plotted against frequency f in (b) in hologarithmic scales. The lines in (b) are the least-squares fit based on the circuit (c) involving a PLC admittance $Y(\omega)=Y_F(\omega/2\pi)^a\{\cos(a\pi/2)+j\sin(a\pi/2)\}$, a dc conductance G_0, a frequency-independent capacitance $C(\infty)$ and an external resistance R_c, with a=0.7, $Y_F=1.9\times10^{-9}$ S sec$^{0.7}$, $G_0=3.6\times10^{-12}$ S, $C(\infty)=7.5\times10^{-10}$ F and R_c=4.3 kΩ.

Fig. 2 shows an example of PLC behavior taken from a merocyanine-fatty acid mixed monolayer sandwiched between Al electrodes. It is noted that the long-time-tail behavior is not confined to the electrial conductions but universal in occurrence.[3,5] It has been reported for various frequency- and time-dependent variables in physico-chemical, biological and socio-economic phenomena.[5]

FUNDAMENTALS OF FRACTAL IMMITTANCE

The admittance of FD is given by $Y(s)=Y_F(a)s^a$ ($0<a<1$) referring to Eq.(1), and the current response to a voltage input defined for $t\geq 0$ is written as

$$i(t) = \frac{Y_F(a)}{\Gamma(-a)}\int_0^t v(t')\,(t-t')^{-a-1}\,dt' \tag{3}$$

where the range of integration is extended down to $-\infty$ if $v(t)\neq 0$ for $t<0$. The range $-\infty \sim 0$ refers to the "null-input response" to govern the memory effect, while $0\sim t$ to the "null-state response" acting as $Y_F(a)d^a/dt^a$ for $t\geq 0$.

The null-input current response is identical with the short-circuit current which is given by

$$i_{sc}(t) = -\frac{Y_F(a)\sin a\pi}{\pi}\int_0^\infty \left\{\int_0^\infty v(-t)e^{-\lambda t}dt\right\}\lambda^a e^{-\lambda t}d\lambda \tag{4}$$

where λ is the relaxation rate and $v(-t)$ refers to the voltage input in the past.[7] Eq.(4) is a two-fold Laplace integral, showing that the one-to-one correspondence is held between $v(-t)$ and $i_{sc}(t)$. Thus, FD is associated with a memory effect in the sense that the entire information on the input in the past is retrievable. The one-to-one correspondence is also held between the current input in the past $i(-t)$ and the open-circuit voltage $v_{oc}(t)$, i.e.,

$$v_{oc}(t) = \frac{Z_F(a)\sin a\pi}{\pi}\int_0^\infty \left\{\int_0^\infty i(-t)e^{-\lambda t}dt\right\}\lambda^a e^{-\lambda t}d\lambda \tag{5}$$

where $Z_F(a)=1/Y_F(a)$.

GUIDELINES OF HARDWARE REALIZATION OF FD

For fabricating practical FD, it is indispensable to lay down guidelines on controlling the value of exponent a. According to the distributed-relaxation -time (DRT) model, the FD admittance is given by a superposition of exponential decay processes with different relaxation rates as

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$$Y(s) = \frac{s\,Y_F(a)\sin a\pi}{\pi}\int_0^\infty \frac{\lambda^{a-1}}{s+\lambda}d\lambda \tag{6}$$

and the FD impedance $Z(s)=1/Y(s)$ by a superposition of exponential saturation as

$$Z(s) = \frac{Y_F(a)^{-1}\sin a\pi}{\pi}\int_0^\infty \frac{\lambda^{-a}}{s+\lambda}d\lambda \tag{7}$$

which are represented by Figs.3(a) and 3(b), respectively.[4,7,8]

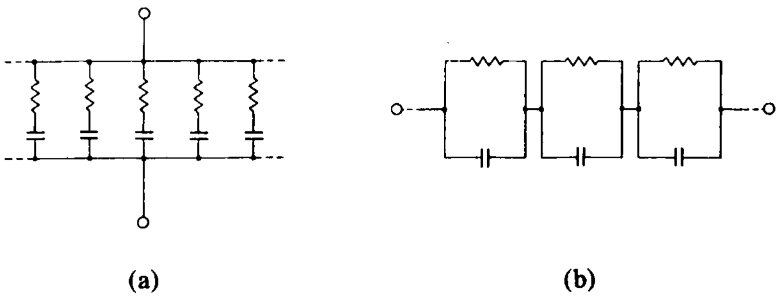

FIGURE 3 Equivalent circuits for FD admittance (a) and FD impedance (b) according to DRT model.

Rotatory dipoles or hopping carriers

Fig.3(a) is compared to a capacitor with rotatory dipoles of different λ in the insulative spacer.[8] The admittance due to the dipoles is given by

$$Y(s) = \frac{s(S/d)}{3k_BT}\int_0^\infty \frac{n(\lambda)\mu(\lambda)^2}{s+\lambda}\lambda d\lambda \tag{8}$$

where S is the electrode area, d the inter-electrode distance, k_BT the thermal energy, and $\mu(\lambda)$ and $n(\lambda)$ denote the magnitude and the density of dipoles, respectively. Eq.(8) shares a common functional form with Eq.(6), and we derive a condition,

$$n(\lambda)\mu(\lambda)^2 = \frac{3k_BTY_F(a)\sin a\pi}{(S/d)\pi}\lambda^{a-2} \tag{9}$$

by referring to Eqs.(6) and (8).[8] It is noted that Eq.(8) applies also to a system of carriers, each hopping between two states, if $\mu(\lambda)$ and $n(\lambda)$ are referred to as the unit charge multiplied by the hopping distance and the carrier density, respectively. Thus, the task is to introduce a well-defined density of guest dipoles or hopping carriers in an insulative thin film. For this purpose, the LB technique is expected to be useful. The polar side groups of guest molecules, for example, may retain the freedom of rotation in the resultant monolayers if the matrix is sufficiently soft.[8]

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Dielectric slabs with graded relaxation times

The FD impedance in Fig.3(b) can be simulated by a leaky capacitor with a multilayered slab.[8] The dielectric relaxation rate $\lambda=1/(\varepsilon\rho)$ is now a function of the depth x along the surface normal, where ε and ρ are the dielectric constant and the resistivity, respectively. If ε is assumed to be constant all over the slab, the impedance can be written as

$$Z(s) = \frac{1}{S}\int_0^\infty \frac{\rho(\lambda)(d\lambda/dx)^{-1}}{s+\lambda}\lambda d\lambda \tag{10}$$

which shares a common functional form with Eq.(7). Thus, we derive a condition

$$\rho(\lambda)(d\lambda/dx)^{-1} = \frac{S\,Y_F(a)^{-1}\sin a\pi}{\pi}\lambda^{-a-1} \tag{11}$$

The task is now reduced to controlling $\rho(\lambda)/(d\lambda/dx)$ for which the LB technique is again expected to be useful. $\rho(\lambda)$ can be modified by introducing "conducting dust" such as metallic fine particles, and $d\lambda/dx$ can be adjusted by stacking different monolayers.[8]

CONCLUSIONS

It has been shown that the fractal immittance device (FD) based on the power-law conductivity (PLC) forms a novel category of circuit elements acting as a non-integer-rank differential/integral operator with a memory effect. The guidelines have been laid down on the hardware realization of FD, for which the LB technique can serve as a useful tool.

The long-time-tail behavior as seen in PLC has been found in various time-dependent variables characterizing physical, chemical, biological and social phenomena. This fact suggests the potential importance of calculations involving the non-integer-rank differentials and integrals for understanding, simulating and controlling those phenomena. Such calculations will be conveniently carried out if we use analogue FD networks.

REFERENCES

1. See, e.g., F.L. Carter (ed), Molecular Electronic Devices (Marcel Dekker, New York, 1982).
2. K. Saito and M. Sugi, Ext. Abstr. 10th Symp. FED (Tokyo, 1992) p.107.
3. See, e.g., A.K. Jonscher, Dielectric Relaxations in Solids (Chelsea Dielectric Press, London, 1983).
4. M. Sugi and K. Saito, IEICE Trans. Fundamentals, E75-A, 720 (1992).
5. M. Sugi and K. Saito, Bul. Electro-tech. Lab., 56, 785 (1992).
6. K. Saito and M. Sugi, IEICE Trans. Fundamentals, E76-A, 204 (1993).
7. M. Sugi and K. Saito, IEICE Trans. Fundamentals, E77-A, 688 (1994).
8. M. Sugi and K. Saito, Thin Solid Films, in press.

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