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Research Article

ELECTRICAL PROPERTIES OF NON-LINEAR ELECTROLYTIC DEVICE DESIGNED USING ACETIC ACID

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ABSTRACT

Until recently, electrical and electronics applications have been focusing on Linear Circuit Elements. However, recent works of scientists have brought the property of nonlinearity to the forefront, proving that it can hold promising applications especially in the field of Chaotic Circuits. Engineering application of nonlinearity is only in inception stage and its time to recognize the material properties with a new perspective.

This brief communication reports an experimental study on Electrical properties of **Non-Linear Electrolytic Device (NLED)** made from Acetic acid which is a weak electrolyte. The above mentioned device exhibits nonlinearity combined with hysteresis in small signal region of Voltage-Current characteristic The NLED manifests variable reactance under condition of high concentration and very low frequency at room temperature. An electrical circuit is plugged using a variable DC power supply, voltmeter and ammeter and the NLED under test. Voltage is varied in steps and corresponding current is recorded. The V-I relation is estimated using Curve fit Toolbox of MATLAB6p5.

Keywords: Non-linearity, Acetic acid, Hysteresis, Chaotic circuit, Electrophoretic effect, Relaxation effect

INTRODUCTION

Electrical and electronics applications are on Linear Circuit Elements; nonlinearity is considered alien and creates distortion and spurious signals. Recent advancements in nonlinearity and chaos open a new field of research. Natural phenomenon occurring in nature is mostly nonlinear and chaotic and research in this field promises to reveal the mysteries of nature.

Chaos is a phenomenon that occurs widely in nonlinear dynamical systems. It may be described as a bounded, periodic, noise-like oscillation; a deterministic system appears to behave randomly and is highly sensitive to initial conditions. The theory of chaos has developed over the past 20 years or so[1], largely in the context of mathematical physics, and has only recently begun to filter through to engineering.

Prof. Chua has designed a simplest electronic chaotic circuit and he says that it must contain at least one non-linear element besides capacitor and inductor[2]. Chaotic circuits have also been implemented using hysteresis property[3].

For decades, electrolytes are being used in cells and batteries as portable electrochemical power source. Electrolytes are also used in electrolytic capacitors. Recently, super capacitors have been designed which use solid electrolytes. Other field of application of electrolytes can be chaotic circuits operating at very low frequency by using **Nonlinear Electrolytic Device (NLED)** made by acetic acid.

Back in 1903, since SA Arrhenius won the Noble award for "Development of the theory of electrolytic dissociation[4]", there has been continuous research to understand the behavior of ions in aqueous solution. Debye–Huckel–Onsager has given the expression (1) for strong electrolytes. Many aspects of this law have been clarified in recent years and studies have been extended to higher concentrations [5-9]. The important problem of motion of ions in the presence of an oscillating electric field has been discussed in [10-16]. However, a fully molecular theory which is valid at high concentrations, even for the simplest case of strong electrolytes, is yet to be developed.

Acetic acid is an organic acid that gives vinegar its sour taste and pungent smell. It is found universally in spoiled foodstuffs, water, and soil. It is a weak acid, in that it is only a partially dissociated acid in an aqueous solution.

Our objective is to characterize acetic acid at very low frequency. In this brief communication we report a concept of nonlinear NLED made of 50% CH_3COOH) solution. The experimental studies demonstrate that reactance of NLED

1. Varies with applied voltage magnitude below breakdown voltage.

2. Varies with frequency of applied voltage.

The experimental data and its manifestation in a graphical manner along with conclusions are presented.

Theory

The motion of ions in an electrolyte solution is usually described by the specific conductivity σ or by the equivalent conductance Λ which is the specific conductivity divided by the molar concentration of the salt. The best known expression for the equivalent conductance of a weak electrolyte solution is the Debye–Huckel–Onsager relation given by[17-18].

$$\Lambda(c) = \alpha\,[\Lambda_o - (A + B\,\Lambda_o)\,\sqrt{\alpha c}] \text{ --(1)}$$

where Λ(c) is the equivalent conductance of the electrolyte when the molar concentration of the salt is c, Λ_o is the conductance at infinite dilution of the electrolyte is the degree of dissociation of ions, A and B are numerical constants which depend on dielectric constant, viscosity, and temperature of the solution and charges of the ions. Constant A accounts for electrophoretic effect and B accounts for relaxation effect.

Every ion is surrounded by a centrally symmetric ionic atmosphere having a resultant charge whose sign is opposite to that of the ion itself. When an e.m.f. is applied the ions tend to move away from its atmosphere. Since the ion and its atmosphere have opposite charges, there is an electrostatic attraction between them, which slows down the motion of ion. The effect on the speed of ion is known as **relaxation effect**[20]. At zero frequency, this relaxation effect leads to the term $B\Lambda_o\sqrt{c}$ in Eq. (1).

When an ion moves in electrolyte solution under finite frequency e.m.f., the atmosphere cannot immediately follow the motion of the central ion, causing a retarding effect on the motion of the ion. This is known as **electrophoretic effect**[20], because it is analogous to that opposing the movement of a colloidal particle in an electric field. Both the ion atmosphere relaxation and the electrophoretic effects are frequency dependent and the two effects result in frequency dependent electrolyte friction $\zeta_{s(\omega)}$ and the conductivity.

Normally, for a weak electrolyte, the value of α is small fraction i.e. 0.132 and for dilute solution concentration c is small value i.e.0.01 N so that the term $\sqrt{\alpha c}$ is approx. 0.01. In such case, the correction factor $(A + B\Lambda_o)\sqrt{\alpha c}$ can be neglected and conductance is given by Eq (2)[20].

$\Lambda(c) = \alpha\Lambda o$--- (2)

The motion of ions in the presence of a time-dependent electric field is traditionally described by the frequency dependent specific conductivity σ (ω) where ω is the oscillation frequency of the external field. The frequency dependent conductivity is intimately related to the frequency-dependent electrolyte friction $\zeta_{s(\omega)}$.

Thus, the total friction on the ion is given by equation (3)[21]. The simple physical interpretation is that an ion diffuses by two mechanisms. The first one is by the random walk caused by its interactions with the surrounding solvent and ion molecules are termed as microscopic friction. The second is the random walk caused by the natural currents or flows present in the liquid and termed as hydroscopic friction. These two contributions to diffusions are additive, as they originate from two different types of motions and are frequency dependent.

$1/\zeta_{s(\omega)} = 1/\zeta_{s;\,mic(\omega)} + 1/\zeta_{s;\,hyd(\omega)}$ ----------------------------------(3)

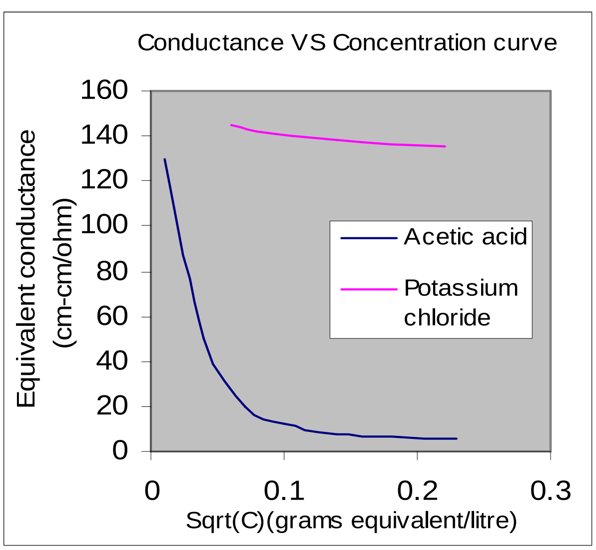
Above Eq (3) holds for dilute solutions. In fact, recent computer simulations have shown that for highly concentrated solutions, the dynamic ion–solvent correlations and the cross velocity correlations are responsible for much of the complex behavior of the conductivity at finite frequencies[19].

In our experiment, we have chosen a weak electrolyte (Acetic acid) at very high concentration (50% by volume) [2].It dissolves in pure water and ionize partially into CH_3COO^- and H_3O^+ ions.

$CH3COOH + H_2O \longleftrightarrow H_3O^+ + CH_3COO^-$ ---------------------------------- (4)

The reaction is reversible and oppositely directed arrows in the equation indicate that equilibrium between molecules and ions is established. Ionization and dissociation of ions is not complete. The conductivity of CH3COOH shows a huge variation with degree of concentration of solution as depicted in Graph1[20]. The macromolecule of CH_3COO^- is surrounded by $H3O^+$ molecules.

As the chosen value of solution concentration c is 16.6 N, therefore the term $\sqrt{\alpha c}$ will have some significant value and the correction factor $(A + B\Lambda_o)\sqrt{\alpha c}$ can not be neglected in our case. The equivalent conductance is will be given by equation (1).



Graph 1: Equivalent Conductance versus Concentration of Electrolyte [20]

It follows that the relaxation effect and electrophoretic effect are much pronounced under given conditions. Also, the unionized molecules of CH3COOH are large in number (due to high concentration solution), which retard the movement of ions.

It follows from above discussions that the reactance (resistance and capacitance) of NLED made by using a weak electrolyte such as acetic acid, must be variable under condition of high concentration and very low frequency.

This research work will be included in the Phd thesis of research scholar Jyoti Gupta (to be submitted to Rani Durgavati University, Jabalpur, M.P.) under the guidance of Dr S. P. Kosta and Dr. P. Mor

MATERIALS AND METHODS

A solution of 50% (by volume) acetic acid in deionized water is prepared in a test tube at 25 ^{0}C. Two probes of copper of diameter 1mm and length 5mm immersed into the solution and kept 5mm apart serve as terminals of NLED.

A circuit is connected using a ScientiFic 4022 digital multimeter connected as voltmeter, a MasTech DT830B digital multimeter is connected as ammeter and APLAB dual variable DC power supply. Voltage is applied from -3 to +3 volts in equal steps and corresponding current is recorded 15 sec after application of each voltage. One complete cycle takes 375 seconds. Therefore frequency of applied signal can be taken as 1/375 sec or 2.66 mHz. Similar reading are taken for time 30 sec and 60 sec. Applied signal frequency is 1.33mHz and 0.66 mHz.Table-1 show Voltage, current and impedence (Z=V/I). Graph 2a represents V-I characteristic and Graph 2b represents V-Z characteristic.

Observation

The V-I curve (Graph 2a) shows that current raises steeply beyond approx. 2.0 volts for positive potential and approx. -2.0 volts for negative potential. Therefore, +2.0 volts and -2.0 volts may be termed as Breakdown voltage.

The V-I curve (Graph 2a) exhibits nonlinearity and hysteresis for small signal between -2.5 to +2.5 volts i.e. forward path of current is different from reverse path. The impedence varies across a large range of 150 kohm to 10 kohm in this range of voltage as shown in Graph 2b. Above +2.5 volts and below -2.5 volts, current varies linearly. The nonlinearity and hysteresis observed in graph 1a is different for different frequency of applied voltage. Hysteresis curve is wider for frequency 2.66 mHz than for 1.33mHz.Hysteresis is lost at 0.66 mHz frequency. The nonlinearity and hysteresis is observed at fractional frequency range.

Mathematical Simulation of Nonlinear V-I Curve Using Matlab

The CURVEFIT TOOLBOX of MATLAB6p5 is used to simulate the relationship between Voltage and Current. The data Voltage V and Current I (at t=15 sec) from Table-1 are used to create workspace in the MATLAB. Then, the GUI of CURVEFIT TOOLBOX is used to fit different mathematical identities to approximate the V-I data. We find that 9th degree polynomial is the nearest and best fit equation for 0 to +3 volts(increasing voltage) and 6th degree polynomial is the nearest and best fit equation for +3 to 0 (decreasing voltage).The curves are shown in Graph 3a and Graph 3b.

Linear model Polynomial 9th degree:

fittedmodel3(x) = p1*x^9 + p2*x^8 + p3*x^7 + p4*x^6 + p5*x^5 + p6*x^4 + p7*x^3 + p8*x^2 + p9*x + p10

Coefficients (with 95% confidence bounds):

p1 = 0.07739 (-0.1281, 0.2829), p2 = 0.2235 (-0.007631, 0.4546)

p3 = -1.295 (-5.242, 2.652), p4 = -3.745 (-7.774, 0.2854)

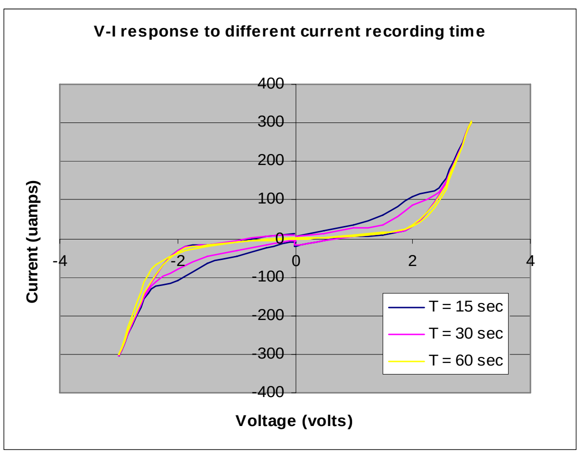
p5 = 7.692 (-17.24, 32.62), p6 = 17.84 (-3.872, 39.56)

p7 = -11.8 (-70.77, 47.17), p8 = -21.17 (-59.5, 17.15)

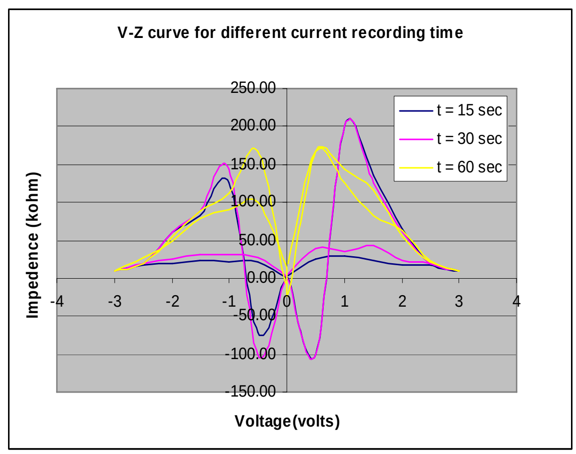
p9 = 22.62 (-20.07, 65.31), p10 = 12.69 (-2.485, 27.87)

Table 1: Voltage, Current and Impedence readings across NLED

voltage V(volts)	current I_1(μA) t = 15 sec	current I_2(μA) t= 30 sec	current I_3 (μA) t= 60 sec	Impedence $Z_1=V/I_1$(kΩ)	Impedence $Z_2=V/I_2$(kΩ)	Impedence $Z_3=V/I_3$(kΩ)
0.02	6	4	0	3.33	5.00	20.00
00.5	20	13	3	25.00	38.46	166.67
1	35	29	8	28.57	34.48	125.00
1.5	62	35	18	24.19	42.86	83.33
2	110	87	32	18.18	22.99	62.5
2.5	142	131	110	17.16	19.08	22.73
3	303	303	303	9.90	9.90	9.90
2.5	123	123	120	20.33	20.33	20.83
2	31	33	36	64.52	60.61	55.56
1.5	11	12	13	136.36	125.00	115.38
1	5	5	7	200.00	200.00	142.86
0.5	-5	-5	3	-100.00	-100.00	166.67
0.02	-19	-15	-1	-1.05	-1.33	-20.00
-0.02	-8	-5	-1	-2.5	4.00	20.00
-0.5	-23	-18	-5	21.75	27.78	100.00
-1	-45	-32	-11	22.22	31.25	90.91
-1.5	-63	-47	-19	23.81	31.91	78.95
-2	-108	-81	-40	18.52	24.69	50.00
-2.5	-143	-134	-93	17.84	18.66	26.88
-3	-305	-303	-302	9.84	9.90	9.93
-2.5	-126	-126	-125	19.84	19.84	20.00
-2	-33	-33	-36	60.61	60.61	55.56
-1.5	-18	-17	-17	83.33	88.24	88.24
-1	-8	-7	-9	125.00	142.86	111.11
-0.5	-7	5	-3	-71.43	-100.00	166.67
-0.02	-12	11	-3	-1.46	-1.82	-6.67



Graph 2a: V-I curve across NLED for one cycle of applied voltage (-3 volts to +3 volts)



Graph 2b-Impedence curve of NLED for one cycle of applied voltage (-3 volts to +3 volts)

[b] A 50 % aqueous solution by volume of Acetic acid is equivalent to 16.6 N concentration.

Goodness[c]

sse: 349.1279 , rsquare: 0.9985 , dfe: 4 , adjrsquare: 0.9953, rmse: 9.3425

Output

numobs: 14 , numparam: 10 , residuals: [14x1 double] , Jacobian: [14x10 double] , exitflag: 1 , algorithm: 'QR factorization and solve'

Linear model Polynomial 6th degree:

fittedmodel2(x) = p1*x^6 + p2*x^5 + p3*x^4 + p4*x^3 + p5*x^2 + p6*x + p7

Coefficients (with 95% confidence bounds):

p1 = -0.09479 (-0.4127, 0.2231), p2 = 1.362 (0.8821, 1.841)

p3 = 2.104 (-2.193, 6.401), p4 = -3.173 (-8.685, 2.338)

p5 = -10.32 (-25.09, 4.454), p6 = 21.72 (7.823, 35.61)

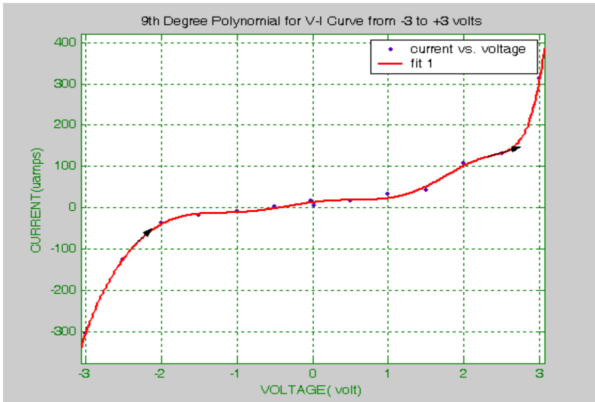
p7 = -8.638 (-19.36, 2.081)

Goodness

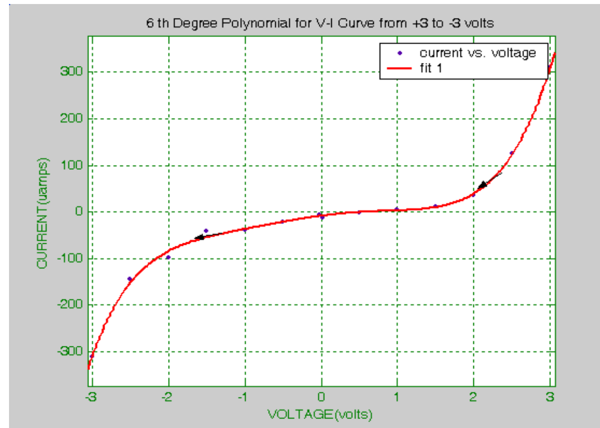
sse: 511.4756 , rsquare: 0.9979 , dfe: 7 , adjrsquare: 0.9961 , rmse: 8.5480

Output

numobs: 14 , numparam: 7, residuals: [14x1 double], Jacobian: [14x7 double] exitflag: 1, algorithm: 'QR factorization and



Graph 3a: MATLAB regression fit curve for increasing voltage from-3V to +3V



Graph 3b: MATLAB regression fit curve for decreasing voltage from +3V to -3V

The Qualitative Interpretation of Observation

Upon application of low potential (-2.0 volts to +2.0 volts) a very small current flows through NLED manifesting a very high impedance state (150-50-kohm). There are only few charge carrier ions, so resistance is high and capacitance is also high (due to high permittivity).An electric field is developed across the terminals. With rising applied voltage, the electric field acts on ionic atmosphere to dissociate more free ions. Thus, the resistance and capacitance gradually decrease.

Capacitance is given by c = ε A/d where A=Area of electrode, D = distance between electrode,

ε = static permittivity

When applied potential increases just above breakdown voltage (-+ 2.0 volts), ions break the bond due to applied electric field and become free to carry charge. Therefore, capacitance reduces and conductance increases. In this region the acetic acid solution exhibits predicted behavior of weak electrolyte.

When applied voltage falls below the breakdown voltage, recombination of ions starts. However, current follows a different curve, other than the rising curve. The recombination dynamics is different from ionization dynamics. A hysteresis is visible below breakdown voltage and small reverse current flows even when the applied voltage becomes zero. The NLED behaves as a nonlinear resistor and nonlinear capacitor in the region below breakdown voltage. Hysteresis observed is due to relaxation effect and electrophoretic effect at low frequency. However, hysteresis is lost at very low frequency i.e. below 0.66 mHz. The ions get enough time for relaxation and adjustment so impedence is same for increasing current and reducing current.

Higher above breakdown voltage, capacitive reactance becomes negligible and impedance becomes constant (approx. 5-10 Kohm). The NLED becomes linear resistor in this region.

Based on above theory, an equivalent circuit for NLED is proposed in fig 1, the reactance Z_{nl} consists of a parallel combination of a variable capacitance C_{nl} and variable resistance R_{nl}.

It may be noted that above characteristic of nonlinearity and hysteresis is exhibited in sub hertz frequency .Above peculiar behavior may be attributed to the dynamic ion–solvent correlations and the cross velocity correlations of the conductivity at finite frequencies and high concentration solution[19].

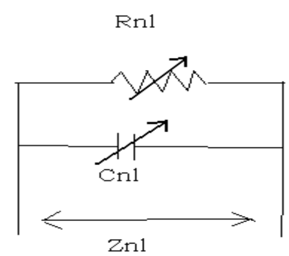


Fig. 1: Equivalent circuit of NLED at 2.66 mHz between +2.5 to -2.5 volts

CONCLUSION

Engineering application of nonlinearity is only in inception stage and its time to recognize the material properties with a new perspective. In this research work, a Nonlinear Electrolytic Device NLED has been realized which exhibits V-I characteristic of 9th degree and 6th degree of nonlinearity combined with hysteresis at sub hertz frequency. The combined property of nonlinearity and hysteresis can make it useful for designing chaotic circuit [2, 3] .It can also be helpful in study of several natural chaotic phenomenons occurring in nature.

The NLED can be designed judiciously as per circuit requirement by varying distance between two probes, by varying probe length, concentration of electrolyte and by selection of electrolyte.

Appendix A

Parameters of curve fitting

solve'c Sse: Sum of squares due to error , rsquare: Coefficient of determination ,dfe: Degrees of freedom, adjrsquare: Degree-of-freedom adjusted coefficient of determination, rmse: Root mean squared error (standard error) ,numobs: Number of observations (response values), numparam : Number of unknown parameters to fit, residuals : Vector of residuals, Jacobian : Jacobian matrix exitflag : Describes the exit condition. If exitflag > 0, the function converged to a solution. If exitflag = 0, the maximum number of function evaluations or iterations was exceeded. If exitflag < 0, the function did not converge to a solution, iterations: Number of iterations used to complete the fit, funcCount : Number of function evaluations used to complete the fit firstorderopt : Measure of first-order optimality, algorithm : Fitting algorithm used.

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