CARBON SUPERCAPACITORS

by

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INTRODUCTION

Carbon supercapacitors store energy in the double layer at the carbon/electrolyte interface. This double layer arises primarily from the electrostatic interaction between electronic charge in the carbon phase and the ions and dipoles in the electrolyte phase. The capacitance of each incremental element of the surface is defined by surface excess concentrations of these mobile charged species, and their corresponding differential excess free energies. Therefore, the capacitance of the carbon interface depends on the composition of the electrolyte.

Carbon has an anisotropic crystal structure consisting of laminates of primarily sp^2 hybridized graphene planes. The size, orientation and crystallographic distortion of these graphitic microcrystals varies from carbon to carbon. However, it is the orientation of the microcrystals with respect to the carbon surface that is of particular importance to carbon supercapacitors. Electrolyte interactions with the hexagonal bonded basal plane of the microcrystals are primarily ion nonspecific and electrostatic in nature as described above. On the other hand, electrolyte interactions with the edge planes of the microcrystals may also involve specific adsorption of ions with partial charge transfer to the carbon surface. As a result, the capacitance of the edge plan carbons is generally much greater than that of the basal plane carbons. Therefore, the crystallographic orientation and accompanying surface chemistry also influences the capacitance of the carbon/electrolyte interface. The double-layer capacitance of the carbon/electrolyte interface has been extensively reviewed by Kinoshita (1).

The double layer capacitance is an extensive property of the interface and, therefore, its magnitude is expected to be proportional to the integrated sum of all the differential surface elements in the carbon electrode. For this reason, supercapacitor electrodes are typically comprised of activated carbons with BET surface areas in excess of 1000 m^2/g. However, the double layer capacitance of activated carbons is rarely proportional to the BET surface area. This discrepancy arises from the geometric distribution of the surface within the pore structure of the electrode. Only surface elements that border electrolyte volume elements of a sufficient size to permit the unconstrained formation of the electrical double layer will be electrochemically active. Carbon surfaces which reside in pores that are narrower than 7-9 Å do not contribute to the double layer capacitance (2,3). The pore geometry also governs the rate of conduction of ions to and from the electrochemically active surface and thereby influences the rate of charge and discharge of the supercapacitor.

It follows from this discussion that carbon supercapacitor electrodes are developed by establishing specific ion interactions at thermodynamically stable surface elements within a pore geometry that maximizes the electrochemically active surface area consistent with the power requirements of the anticipated application. In a practical sense, these properties are manifest in three figures of merit: 1) the volume specific capacitance (C_v, in F/cm^3) of the porous carbon electrode, 2) the effective series resistance (ESR, in Ωcm^2) of the supercapacitor, and 3) the voltage limit of each cell in the supercapacitor.

Whereas the volume specific capacitance and voltage limit may be considered fundamental properties of the specific carbon electrode in a specific electrolyte, the effective series resistance represents a consolidation of extensive and intensive properties including the electrical resistivity of the carbon, the ionic resistivity of the electrolyte, the pore geometry of the carbon, the pore geometry of the separator, and the thicknesses of the carbon electrodes and separator. The ESR depends on cell design. The volume specific capacitance and voltage limit do not.

The measurement of C_V and ERS will be described first. Next, the significance of ESR in the utilization of the supercapacitor will be discussed. And, finally, the status of selected researchers and developers of supercapacitors throughout the world will be presented. Since ESR depends on cell design, the status report will be based on volume specific capacitance and voltage limit only.

MEASUREMENT OF CAPACITANCE AND EFFECTIVE SERIES RESISTANCE

Supercapacitors are typically represented by an equivalent circuit consisting of a capacitor C in series with a resistor R_S. For this equivalent circuit, shown in Figure 1, the capacitance C is give by equation [1]:

$$C = \frac{Q}{V_C} \qquad [1]$$

where: Q = charge stored on the plates of the capacitor
V_C = voltage drop across the capacitor

Differentiation of equation [1] with respect to time yields:

$$C = i\frac{dt}{dV_C} \qquad [2]$$

where: $i = \frac{dQ}{dt}$ = current

The energy stored in the capacitor is defined by equation [3]:

$$E_C = \frac{1}{2}CV_C^2 \qquad [3]$$

The complex impedance of the series R_SC equivalent circuit is given by equation [4]:

$$Z = R_S - \frac{j}{\omega C} \qquad [4]$$

where: ω = the radian frequency $\omega = 2\pi f$,

$j = \sqrt{-1}$

in general: $Z = R + jX$

where: R = Resistive component and
X = Reactive (imaginary) component

The frequency dispersion of the complex impedance of this supercapacitor equivalent circuit is also shown in Figure 1. Applying equation [4], the effective series resistance, R_s, is equal to the high frequency intercept with the resistance axis *, and the capacitance is obtained from the reactive component at a selected frequency ω using equation [5]:

$$C = \frac{1}{\omega X} \qquad [5]$$

Since the capacitor in our equivalent circuit is an ideal capacitor, its capacitance is independent of frequency , and equation [5] can be used to determine the capacitance at any frequency at which the reactance can be measured. When the capacitance is not ideal, the value computed using equation [5] will depend upon the frequency at which the reactance is measured, and the impedance plot may also be skewed with respect to the vertical plot shown in Figure 1.

It is also possible to measure R_S and C of the equivalent circuit in the time domain by applying a constant charging (or discharging) current to the circuit as shown in Figure 2. The voltage-time response will yield a straight line with slope dV/dt equal to i/C according to equation [2], and intercept equal to $V_R = iR_s$ at t=0. Additionally, the capacitance may be computed using equation [1] in which the charge Q is obtained from the integration of the current from t=0 to t , and the voltage is compensated for the loss across the R_s ie. $V_C=V-V_R$.

The total energy, E_T, required to charge this ideal supercapacitor to a cutoff voltage V is equal to the area under the curve (Figure 2) multiplied by the current i. A fraction of this energy, E_R , will be dissipated as heat across R_s according to equation [6]:

$$E_R = i\,V_R\,t \qquad [6]$$

and the remaining energy, E_C , will be stored in the capacitor.

Figures 1 and 2 and equations [1] through [6] do not describe the behavior of carbon supercapacitors at high frequencies or high charge/discharge rates. The series R_sC equivalent circuit is a good approximation for each incremental carbon surface element, however, these surface elements are distributed throughout the porous network of the electrode, and the simple circuit in Figure 1 does not account for this distribution. If the

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* For a series R_SC equivalent circuit consisting of ideal circuit elements, the complex impedance is a vertical line as shown in Figure 1, and R_s can be determined from the resistive component of Z at any frequency. If the capacitance is not ideal, or if another circuit element is added to the circuit to accommodate other physical or electrochemical processes (which will not be discussed in this text) then the impedance plot will be skewed or completely altered at lower frequencies. In this case , R_s must be obtained from the high frequency intercept.

pores in the carbon electrode are visualized as cylindrical capillaries of radius r and length l, then the differential elements of surface area that line the inside walls of these capillaries are distributed throughout the electrode in the same manner that capacitance is distributed in a transmission line.(4)
Therefore, the transmission line equivalent circuit shown in Figure 3 is a better representation of a carbon electrode when the pore geometry can be approximated by this capillary model. The complex impedance of this semi-infinite cylindrical porous carbon electrode is given by equation [7](4,5):

$$Z_p = \frac{(1-j)}{2\pi n\sqrt{r^3\kappa\omega C_{dl}}} \coth\left[l(1+j)\sqrt{\frac{\omega C_{dl}}{\kappa r}}\right] \qquad [7]$$

where:
κ = electrolyte conductivity
r = effective pore radius
n = effective pore number
l = effective pore length
C_{dl} = double layer capacitance

Equation [7] is plotted in Figure 3. At high frequency, equation [7] reduces to equation [8]:

$$Z_p = \frac{(1-j)}{2\pi n\sqrt{r^3\kappa\omega C_{dl}}} \qquad [8]$$

$$\text{for:} \quad l\sqrt{\frac{\omega C_{dl}}{\kappa r}}(1+j) > 3$$

At low frequencies, equation [7] reduces to equation [9]:

$$Z_p = \frac{l}{\pi r^2 n\kappa} - \frac{j}{2\pi rnl\omega C_{dl}} = \Omega - \frac{j}{\omega C} \qquad [9]$$

$$\text{for:} \quad l\sqrt{\frac{\omega C_{dl}}{\kappa r}}(1+j) < 0.1$$

$$\text{where } \Omega = \frac{l}{\pi r^2 n\kappa} \qquad [10]$$

$$X = \frac{-1}{2\pi rnl\omega C_{dl}} = \frac{-1}{\omega C} \qquad [11]$$

$$C = SC_{dl} = \text{low frequency capacitance} \qquad [12]$$

$$S = 2\pi r l n = \text{electrochemically active surface area} \quad [13]$$

According to the capillary model of the pore structure, the total pore volume of an electrode is given by equation [14]:

$$V_e = \pi r^2 l n = \text{total pore volume} \quad [14]$$

Therefore, when the complex impedance of a porous carbon electrode resembles Figure 3, a complete characterization of the pore structure of the electrode can be made with respect to the simple capillary model described above. For this analysis, one must independently know the total pore volume, V_e, of the electrode, and one must know the double layer capacitance, C_{dl}, of the carbon surface. From the reactance at low frequency (equation [11]) one obtains the electrode supercapacitance C. The supercapacitance, C, is used to compute the total electrochemically active surface area using equation [12]. The effective pore radius, effective pore length, and effective pore number are then computed using equations [15], [16], and [17] respectively:

$$r = \frac{2V_e}{S} = \text{effective pore radius} \quad [15]$$

$$l = \sqrt{\kappa \Omega V_e} = \text{effective pore length} \quad [16]$$

$$n = \frac{S}{2\pi r l} = \text{effective pore number} \quad [17]$$

This model completely ignores the geometric details and electronic resistance of the carbon pore structure. All pores are assumed non intersecting right circular cylinders of equal and uniform radius, length, volume, and surface area. This model also assumes a homogeneous carbon surface contrary to the discussion of the anisotropic properties of carbon surfaces in the introduction of this report. Nevertheless, this model provides a basis for the comparison of the charge/discharge behavior of supercapacitor electrodes, and relates this behavior to effective geometric parameters which approximate the electrode pore structure.

Figure 4 shows the voltage-time response of the transmission line equivalent circuit of Figure 3 to a current step. Comparison of Figure 4 with Figure 2 shows that the voltage transient for charging a transmission line equivalent circuit is very similar to that for a series R_sC circuit, except that the voltage of the transmission line circuit does not initially respond to the current step as rapidly as the simple R_sC circuit, and, the effective series resistance now has an added component, Ω, which represents the sum of all the resistive electrolyte volume elements in the pore structure of the carbon electrode.. As with Figure 2, the energy required to charge the transmission line equivalent circuit to a cutoff voltage V is equal to the area under the curve multiplied by the current i. It is apparent from Figure 4 that the energy stored by the capacitor is not $E_C = \frac{1}{2}CV_C^2$. Instead, E_C must be corrected for the non-uniform charging of the distributed capacitance elements in the electrode. This energy loss is designated E_{CL} in Figure 4. Therefore, for the transmission line equivalent circuit:

$$E_C = \frac{1}{2}CV_C^2 - E_{CL} = \frac{1}{2} i V_C t - E_{CL} \qquad [18]$$

It also follows from Figure 4 that the energy loss due to resistance heating of the electrolyte, E_R, in the separator and carbon pore structure is not $E_R = iV_{ESR}\,t$. Instead, resistive energy loss in the electrolyte phase is given by:

$$E_R = i V_{ESR}\, t - E_{RL} \qquad [20]$$

where: $$V_{ESR} = iR_s + i\Omega \qquad [21]$$

Under identical test conditions, the transmission line equivalent circuit will store less energy than a simple series $R_{ESR}C$ circuit in which $R_{ESR} = R_s + \Omega$, and C is equal to the sum of all capacitive elements in the transmission line. If one attempts to describe a supercapacitor electrode using a simple $R_{ESR}C$ circuit, then the effective capacitance and effective series resistance will appear to decline as the charge/discharge current is increased or as the frequency is increased. In fact, neither the capacitance nor the resistance changes. Instead, the pore structure of the electrode limits the rate at which the individual capacitive elements can be charge or discharge. The apparent decline in capacitance is the result of non-uniform (less efficient) utilization of the carbon surface at high charge/discharge rates or high frequency.

In order to obtain an explicit expression for the energy efficiency of the charge/discharge behavior of the transmission line equivalent circuit, one must integrate the area E_{CL} + E_{RL} in Figure 4. The time domain voltage response of the transmission line equivalent circuit is obtained from the inverse Fourier transform of equation [7]. Since an explicit inverse transform of this equation is not available, an explicit expression for $E_{CL} + E_{RL}$ is also not available. Instead, these energies must be obtained by digital inverse Fourier transform. This approach will not be pursued in this text. Instead, we will limit the discussion of energy efficiency to the simple series R_sC circuit shown in Figure 2. This discussion applies only when $E_{CL} + E_{RL} << \frac{1}{2}CV_C^2$. For these conditions, the charging efficiency is given by equation [22]:

$$\text{charging efficiency} = \Psi_C = \frac{\text{Energy stored}}{\text{Energy input}} = \frac{E_C}{E_C + E_R} \qquad [22]$$

Substituting equations [3] and [6] into equation [22] yields equation [23]:

$$\Psi_C = \frac{V - V_R}{V + V_R} \qquad [23]$$

Similarly, the round trip energy efficiency, Ψ_D, during charge/discharge cycling at constant current is given by equation [24]:

$$\Psi_D = \frac{V - 2V_R}{V + 2V_R} \qquad [24]$$

Since $V_R = i R_s$, the energy efficiency of the ideal supercapacitor is a simple function of the current, the cutoff voltage, and the effective series resistance.

In this section we have described the frequency domain and time domain behavior of two circuits that approximate the electrical behavior of carbon supercapacitors. The transmission line equivalent circuit is a better approximation over all frequencies and currents, however, the mathematical complications in the transformation from the frequency domain to the time domain, for this model, precludes the derivation of explicit expressions for energy storage and dissipation in this equivalent circuit. Because of these complications, it is a general practice to represent a supercapacitor as a simple series $R_{ESR}C$ circuit, and downgrade the effective capacitance and effective series resistance at high current or high frequency where the model does not actually apply.

The equivalent circuits that are used in this section are composed if *ideal* capacitors and/or capacitor elements which do not vary with frequency or voltage. The electrochemical behavior of the edge planes of the carbon surface, however, can lead to a voltage dependence of the capacitance. When this occurs, the voltage transients described in Figures 2 and 4 are nonlinear, and the charge curve may not be symmetric with respect to the discharge curve. Under these circumstances the simple time domain analysis presented in this section is no longer valid. Nevertheless, the functional relationship between the capacitance and the voltage can be obtained from measurements of the complex impedance of the electrode as a function of voltage. And, using the same complex impedance measurements, R_{ESR} can be resolved into R_s and Ω components thus suggesting cell design or pore structure modifications needed to optimize energy transfer in particular applications.

COMPARISON OF CARBON SUPERCAPACITOR ELECTRODES

Supercapacitors are made from a variety of carbons in a variety of electrolytes. Selected carbons include activated powders, fibers, and foams as well as sinter-fused composites. It is anticipated that the variety of surface chemistries and pore structures exhibited by these carbons would lead to a spectrum of performance characteristics, and that certain carbons would yield superior performance. In the previous section we have shown that the performance of supercapacitor electrodes can be described under limited circumstance by C, R_{ESR} and the voltage limit. The effective series resistance of the surercapacitor is a very important figure of merit which limits the charge/discharge rate and efficiency of the supercapacitor. This property depends on the pore structure of the carbon, however, it is also a strong function of electrode thickness, electrolyte resistivity, and separator thickness and porosity. The ESR of a supercapacitor depends heavily on cell design and, therefore, on the intended application. For this reason, it is not a good figure of merit for the relative comparison of carbon materials. The capacitance, C_V, and the voltage limit, V, of the supercapacitor, on the other hand, are extensive properties of the carbon electrodes in specific electrolytes. These properties provide a better (if not complete) basis for the comparison of carbon supercapacitor electrodes.

Table I is a compilation of C_V and voltage limits for selected supercapacitor technologies. It was not possible in every case to obtain the precise volume of each carbon electrode from the cited publication. When this information was not available the electrode volume was estimated from other information (such as carbon density or total cell volume) that was provide. This approximation is indicated with ~). None of the authors that are reference in Table I discussed the voltage dependence of the capacitance. Instead an effective capacitance was reported for the maximum voltage range of each device. For all calculations, both electrodes in each device were assumed to have equal volumes and equal thicknesses

SUMMARY

Carbon supercapacitors are represented as distributed RC networks with transmission line equivalent circuits. At low charge/discharge rates and low frequencies these networks approximate a simple series $R_{ESR}C$ circuit. The energy efficiency of the supercapacitor is limited by the voltage drop across the ESR. The pore structure of the carbon electrode defines the electrochemically active surface area which in turn establishes the volume specific capacitance of the carbon material. To date, the highest volume specific capacitance reported for a supercapacitor electrode is 220 F/cm^3 in aqueous H_2SO_4 (10) and ~60 F/cm^3 in nonaqueous electrolyte (8).

ACKNOWLEDGEMENT

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FIGURE LEGENDS

Figure 1. Complex impedance of a simple series R_sC equivalent circuit.

Figure 2. Time domain response of simple series R_sC equivalent circuit to a current step. E_c is the energy stored in the capacitor, and E_R is the energy dissipated across the series resistor

Figure 3 Complex impedance of a transmission line equivalent circuit.

Figure 4 Time domain response of a transmission line equivalent circuit shown in Figure 3 to a current step. E_C is the energy storred in the capacitor elements of the distributed network, and E_R is the energy dissipated across the resistive elements of the circuit. E_{CL} is the energy that was not stored and E_{RL} is the energy that was not dissipated in the circuit because of the nonuniform distribution of the current within the network.

DISCLAIMER

TABLE I
Carbon Supercapacitor Electrodes
Current Status

Author	Affiliation	Ref.	Electrolyte	Voltage Limit	C_v F/cm^3
Yoshida et al	Matsushita	6	PC-TEATFB	2.3	16
Sugimoto	Seiko	7	organic	2.5	~3
Morimoto	Asahi Glass	8	PC-TEPTFB	3.0	~60
Sawada et al	Isuzu/Fuji	9	H_2SO_4	1.0	~30
Kibi et al	NEC	10	H_2SO_4	1.0	220
Miller	Evans	11	H_2SO_4	1.0	125
Blank et al	Maxwell	12	KOH	1.0	67
Mayer et al	LLNL	13	KOH	1.0	105
Delnick et al	SNL		KOH	1.0	125

LLNL = Lawrence Livermore National Laboratories
SNL = Sandia National Laboratories

PC = Propylene Carbonate
TEATFB = tetraethylammonium tetrafluoroborate
TEPTFB = tetraethylphosphonium tetrafluoroborate

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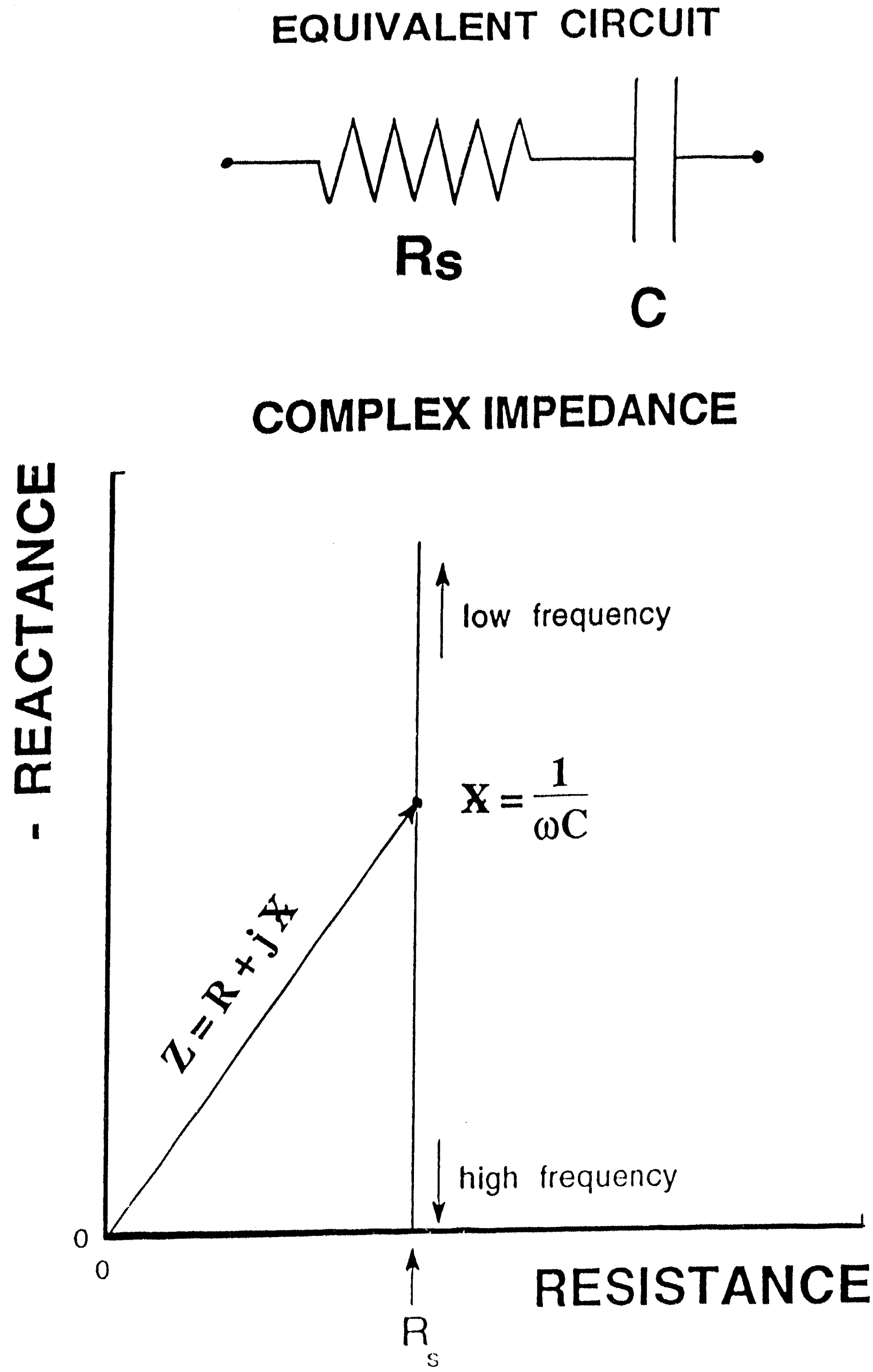
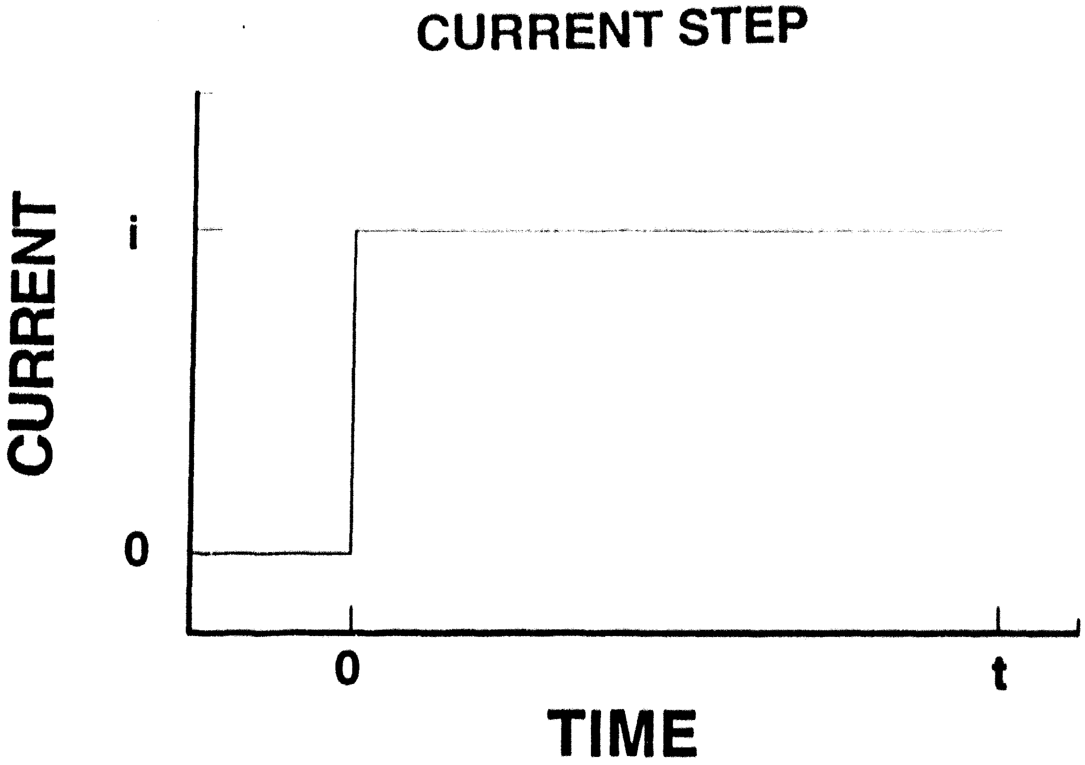

EQUIVALENT CIRCUIT
Rs
C
COMPLEX IMPEDANCE
- REACTANCE
low frequency
$X = \frac{1}{\omega C}$
$Z = R + jX$
high frequency
0
0
RESISTANCE
R_s

FIG 1


CURRENT STEP

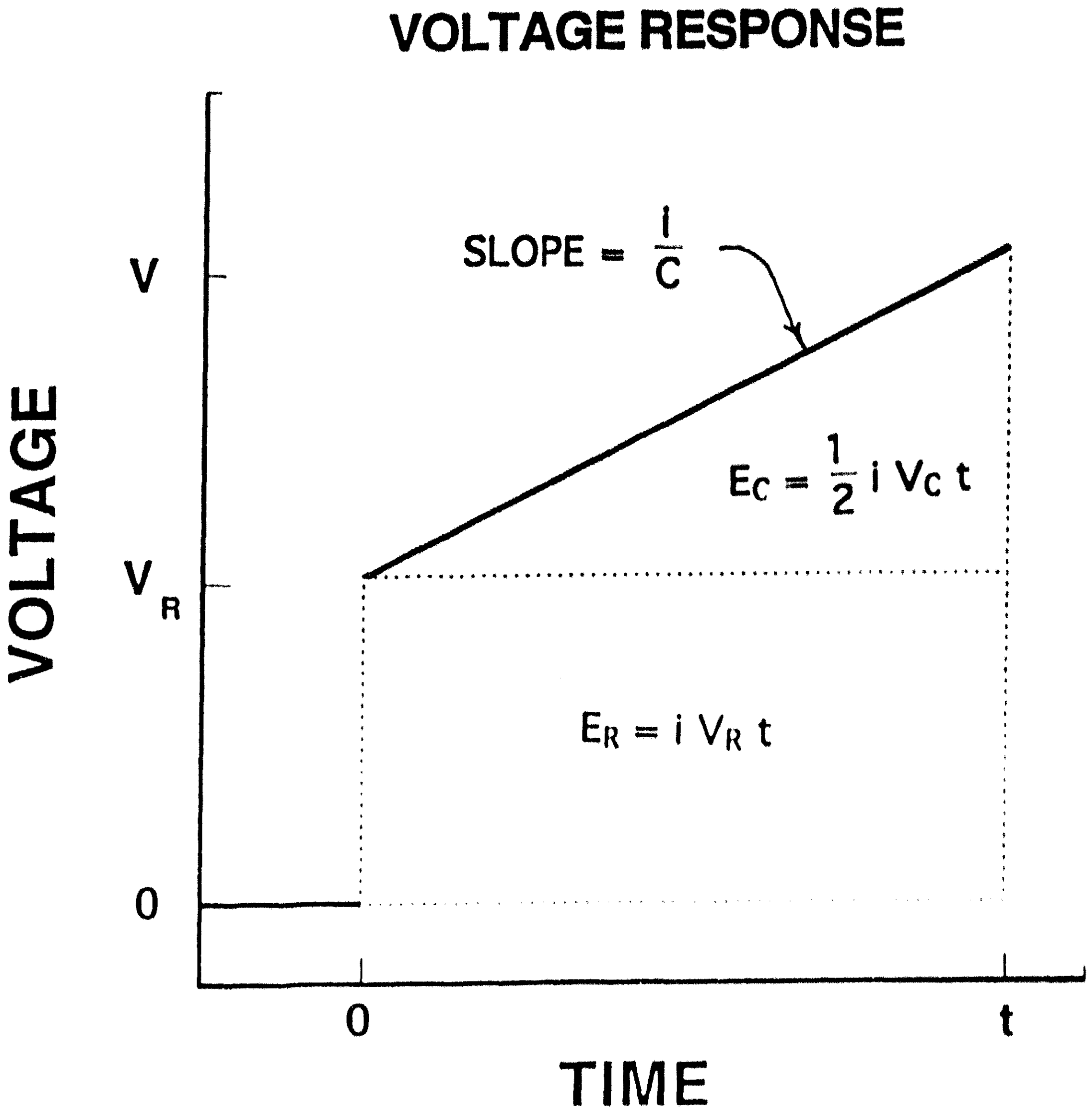
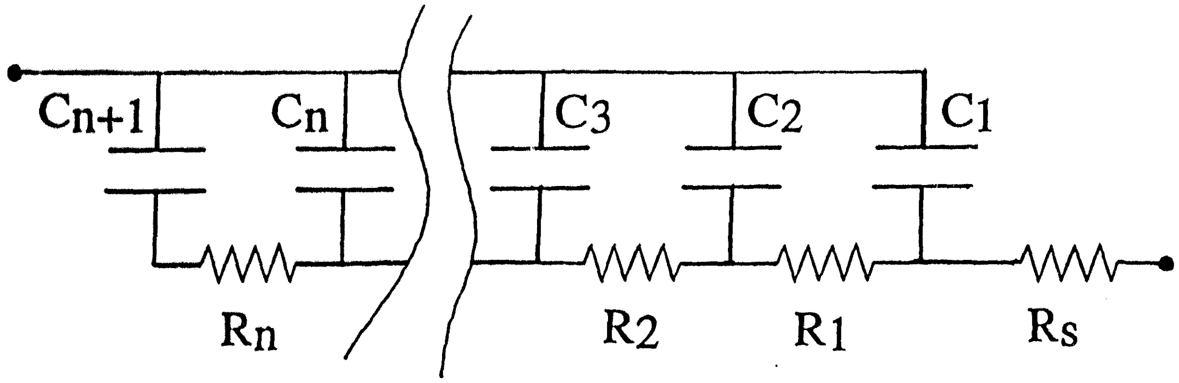

VOLTAGE RESPONSE

Fig. 2.

EQUIVALENT CIRCUIT



$$\sum R_n = \Omega \qquad \sum C_n = C$$

COMPLEX IMPEDANCE

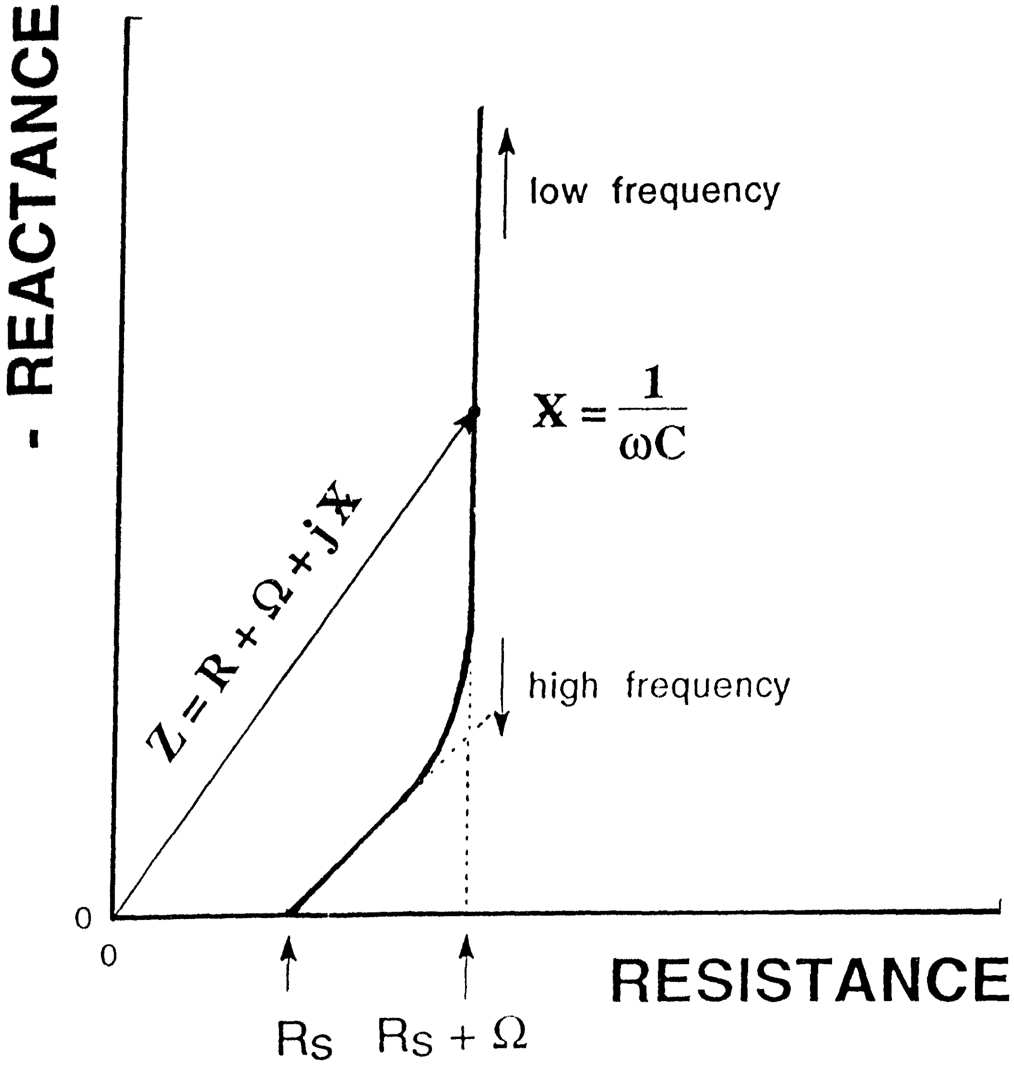


FIG. 3

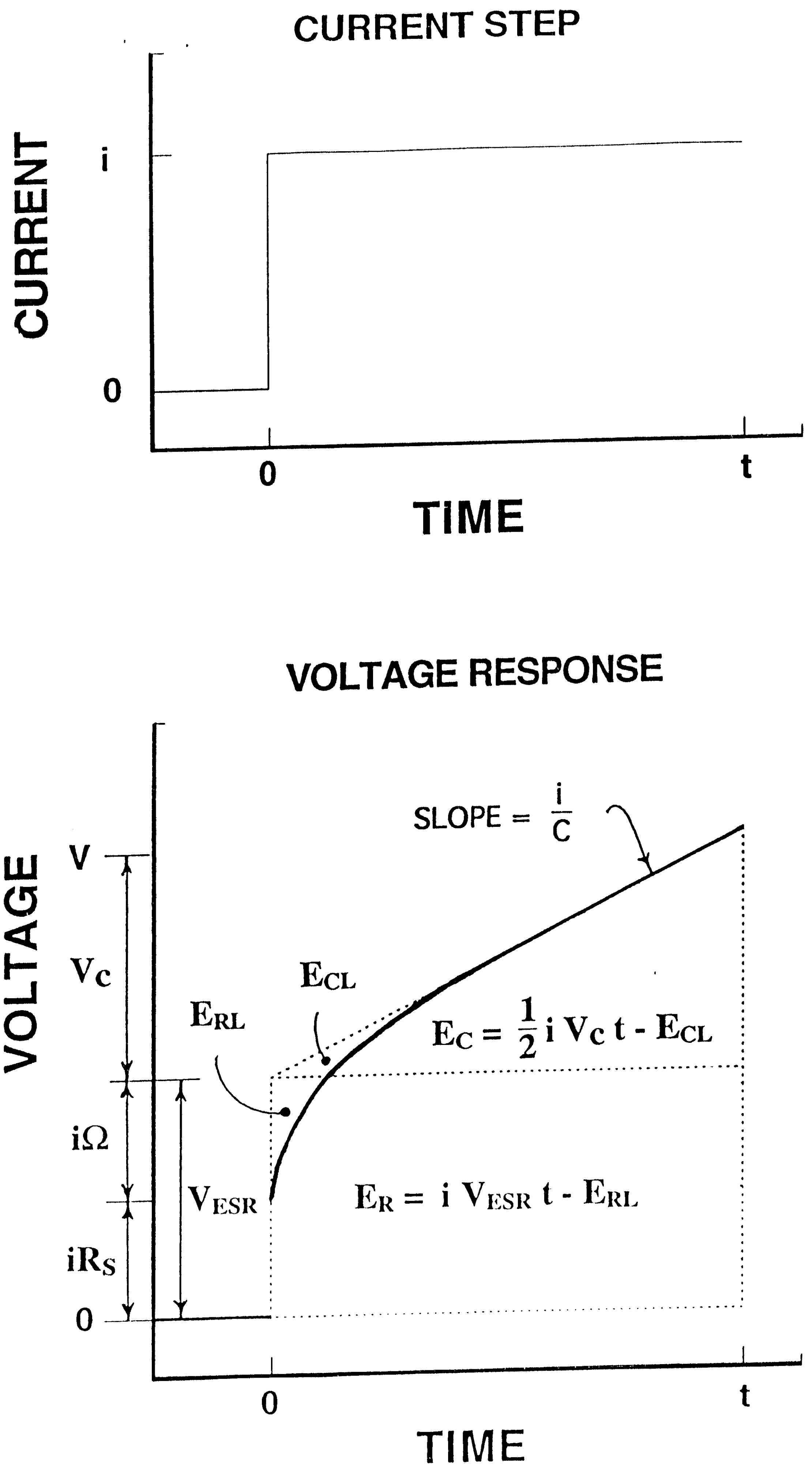

CURRENT STEP
CURRENT
i
0
0
t
TIME
VOLTAGE RESPONSE
VOLTAGE
SLOPE = $\frac{i}{C}$
V
V_C
E_{CL}
E_{RL}
$E_C = \frac{1}{2} i V_C t - E_{CL}$
$i\Omega$
V_{ESR}
$E_R = i V_{ESR} t - E_{RL}$
iR_S
0
0
t
TIME

FIG 4

END

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