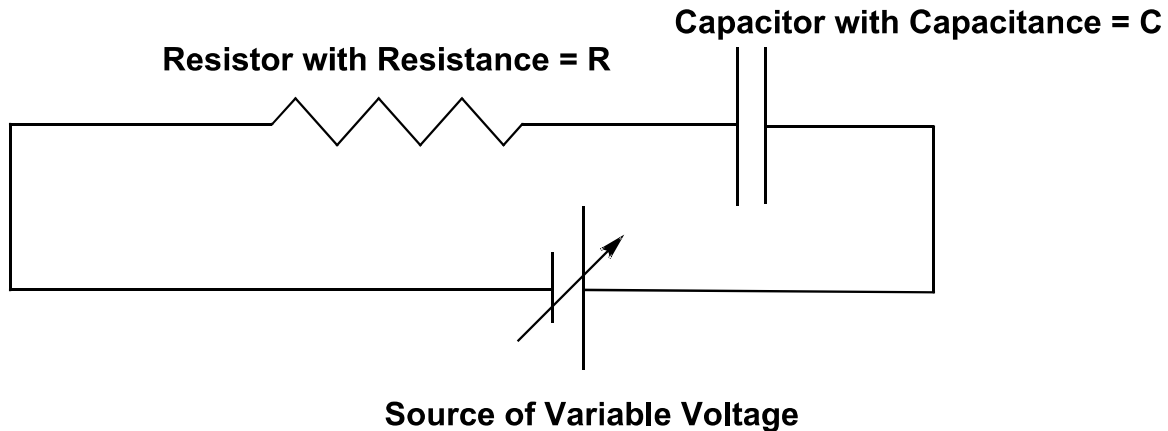
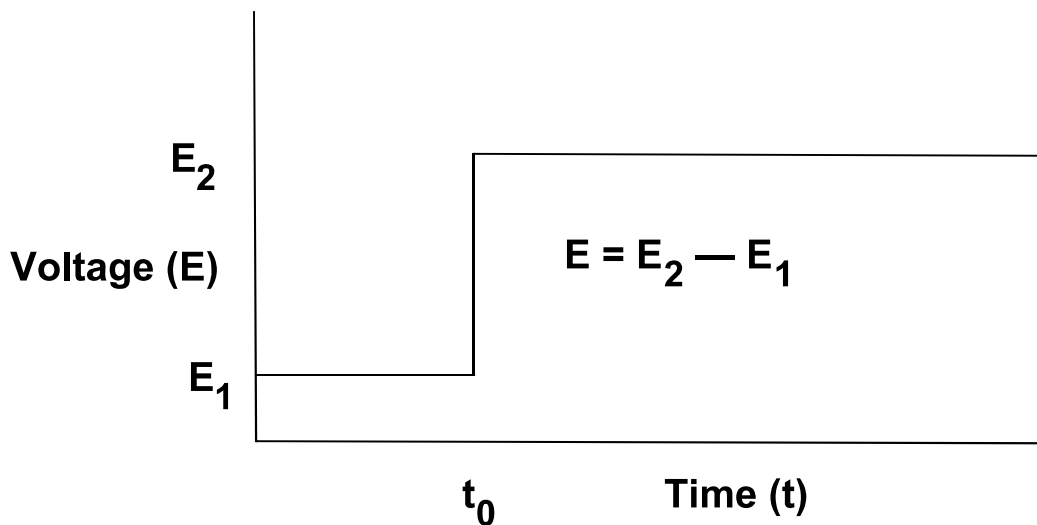


**Simple RC Circuit Model of Working Electrode:**

$E$  = applied potential (Volts, Joules/Coulomb)  
 $R$  = circuit resistance (Ohms, Joules-Sec/Coulomb<sup>2</sup>)  
 $i$  = circuit current (Amps, Coulombs/Sec)  
 $q$  = charge on capacitor (Coulombs)  
 $C$  = capacitance (Coulombs/Volt, Farad)

*Potential Pushing Current in Circuit* =  $E_R = iR(i) = iR$       assume  $R$  is a constant

*Potential Charging the Capacitor* =  $E_C = \frac{q}{C(q)} = \frac{q}{C}$       assume  $C$  is a constant

**Apply a potential (voltage) step:****Current as a function of time for voltage step ( $E_1$  = rest potential):**

$$E = E_R + E_C = iR + \frac{q}{C}$$

$$i = \frac{E}{R} - \frac{q}{CR}$$

$$\frac{dq}{dt} = \frac{-q}{CR} + \frac{E}{R} = \left(\frac{-1}{CR}\right)(q - EC)$$

$$\int_0^q \frac{dq}{(q - EC)} = - \int_0^t \frac{dt}{CR}$$

$$\ln(q - EC) = \frac{-t}{CR} + k(\text{constant of integration})$$

$$q - EC = \left(e^{\left(\frac{-t}{CR}\right)}\right)(e^k)$$

Boundary Condition:  $q = 0$  at  $t = 0$

$$-EC = e^k$$

$$q - EC = (-EC)e^{\left(\frac{-t}{CR}\right)}$$

$$q = (EC) \left(1 - e^{\left(\frac{-t}{CR}\right)}\right)$$

$$\boxed{\frac{dq}{dt} = i = \frac{E}{R} e^{\left(\frac{-t}{CR}\right)}}$$

Collect data points for current as a function of time after application of the voltage step (E). Note that the unit of "CR" (capacitance x resistance) is time. "CR" is known as the time constant of the cell. Take the natural log of both sides of the equation;

$$\ln(i) = \ln\left(\frac{E}{R}\right) - \left(\frac{1}{CR}\right)t$$

Carry out a linear regression of the natural log of the current versus the time. The slope of the regression provides the time constant "CR". The y-intercept of the regression provides the cell resistance (E is known). With the cell resistance, the capacitance of the working electrode can be determined.

$$m = \text{slope} = \frac{-1}{CR} \quad b = y \text{ intercept} = \ln\left(\frac{E}{R}\right)$$

$$R = \frac{E}{e^b} \quad CR = \frac{-1}{m} \quad C = \frac{-1}{mR} = \frac{-e^b}{mE} \quad b \text{ is positive, } m \text{ is negative}$$

If the area of the working electrode is known, then the total capacitance can be converted to capacitance per unit area. The capacitance per unit area provides information concerning the structure the double layer on the particular working electrode under investigation. Note that the capacitance of an electrode is a function of the potential, and the capacitance measured by this method is the change in capacitance that occurs on going from the initial potential to the final potential of the potential step. This information helps to better understand the surface structure of the electrode in a polarized state. Note that this analysis assumes the electrode is an IPE (ideal polarized electrode) wherein no faradaic current flows in the potential range under examination.

**Apply a potential (voltage) ramp:**

$E_0$  = initial applied potential (Volts)

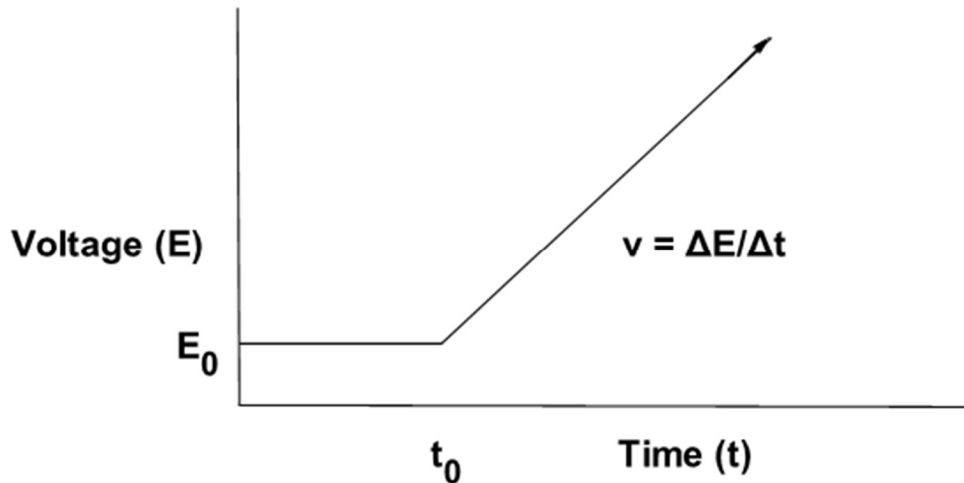
$v$  = constant time rate of applied potential change (Volts/Sec)

$R$  = circuit resistance (Ohms)

$i$  = circuit current (Amps, Coulombs/Sec)

$q$  = charge on capacitor (Coulombs)

$C$  = capacitance (Coulombs/Volt, Farads)



Current (i) as a function of time (t) for voltage ramp ( $E_0$  = rest potential):

$$E = E_0 + vt = E_R + E_C = iR + \frac{q}{C}$$

$$E_0 + vt = iR + \frac{q}{C}$$

$$\frac{dq}{dt} = \frac{E_0}{R} + \frac{vt}{R} - \frac{q}{RC}$$

$$\frac{dq}{dt} = -\frac{q}{RC} + \frac{vt}{R} + \frac{E_0}{R} = -aq + bt + c$$

$$a = \frac{1}{RC} \quad b = \frac{v}{R} \quad c = \frac{E_0}{R}$$

$$\frac{dq}{dt} + aq = bt + c$$

$$\mu(x) = e^{at}$$

$$(e^{at}) \frac{dq}{dt} + aq(e^{at}) = (-e^{at})(-bt - c)$$

$$a(e^{at}) = \frac{d}{dt}(e^{at})$$

$$(e^{at}) \frac{dq}{dt} + \frac{d}{dt}(e^{at})q = (-e^{at})(-bt - c)$$

$$f \frac{dg}{dx} + g \frac{df}{dx} = \frac{d(fg)}{dx} \quad \text{reverse product rule}$$

$$(e^{at}) \frac{dq}{dt} + \frac{d}{dt}(e^{at})q = \frac{d}{dt}(qe^{at}) = (-e^{at})(-bt - c)$$

$$\int_0^t \frac{d}{dt}(qe^{at})dt = \int_0^t (-e^{at})(-bt - c)dt$$

$$\int_0^t (-e^{at})(-bt - c)dt = \int_0^t (bt + c)(e^{at})dt$$

$$\int fg' = fg - \int f'g$$

$$f = bt + c \quad g' = e^{at}$$

$$\int (bt + c)(e^{at})dt = (bt + c) \left( \frac{e^{at}}{a} \right) - \int \frac{be^{at}}{a} dt$$

$$\int \frac{be^{at}}{a} dt = \int \frac{be^u}{a} \frac{du}{a} = \frac{b}{a^2} \int e^u du = \frac{be^{at}}{a^2} \quad u = at$$

$$\int (bt + c)(e^{at}) dt = (bt + c) \left( \frac{e^{at}}{a} \right) - \int \frac{be^{at}}{a} dt = \frac{(bt + c)e^{at}}{a} - \frac{be^{at}}{a^2}$$

$$\frac{(bt + c)e^{at}}{a} - \frac{be^{at}}{a^2} = \frac{e^{at}(a(bt + c) - b)}{a^2}$$

$$qe^{at} = \frac{e^{at}(ac + b(at - 1))}{(a)^2} + k \quad (\text{constant of integration})$$

$$q = \frac{ac + bat - b}{(a)^2} + ke^{-at}$$

$$q = \frac{-b}{a^2} + \frac{c}{a} + \frac{bt}{a} + ke^{-at}$$

$$q(0) = 0 = \frac{-b}{a^2} + \frac{c}{a} + k \quad k = \frac{b}{a^2} - \frac{c}{a} = \frac{b - ac}{a^2}$$

$$q = \frac{-b}{a^2} + \frac{c}{a} + \frac{bt}{a} + \left( \frac{b - ac}{a^2} \right) e^{-at}$$

$$a = \frac{1}{RC} \quad b = \frac{v}{R} \quad c = \frac{E_0}{R}$$

$$\frac{b - ac}{a^2} = \frac{\frac{RC^2v}{C^2R^2} - \frac{CE_0}{R^2C^2}}{\frac{1}{R^2C^2}} = vC^2R - CE_0$$

$$q = -vRC^2 + CE_0 + vCt + (vC^2R - CE_0)e^{-\left(\frac{t}{RC}\right)}$$

Take the derivative with time:

$$\frac{dq}{dt} = vC + \left(\frac{-1}{RC}\right)(vC^2R - CE_0)e^{-\left(\frac{t}{RC}\right)}$$

$$\boxed{\frac{dq}{dt} = i = vC + \left(\frac{E_0}{R} - vC\right)e^{-\left(\frac{t}{RC}\right)}}$$

This equation can't be linearized as is, but one can proceed as follows.

$$i = vC + \left(\frac{E_0}{R} - vC\right)e^{-\left(\frac{t}{RC}\right)} = a + be^{ct} \quad a = vC \quad b = \left(\frac{E_0}{R} - vC\right) \quad c = -\left(\frac{1}{RC}\right)$$

We now take a step backwards and integrate. Note that the integral of current over time equals the charge (q) passed.

$$\int idt = \int a dt + \int be^{ct} dt$$

$$\int idt = q = at + \frac{b}{c}e^{ct} + k \text{ (constant of integration)}$$

$$q = at + \frac{b}{c}e^{ct} + k \quad q = 0 \text{ at } t = 0 \quad k = -\frac{b}{c}$$

$$q = at + \frac{1}{c}(be^{ct} + a) - \frac{a}{c} - \frac{b}{c} = at + \frac{1}{c}(i) - \frac{1}{c}(a + b) \quad -\frac{1}{c}(a + b) = CE_0$$

$$q = at + \frac{i}{c} + CE_0 \quad i = cq - act - cCE_0 = -\left(\frac{q}{RC}\right) + \frac{v}{R}t + \frac{E_0}{R}$$

$$i = \frac{(E_0 + vt)}{R} - \left(\frac{q}{RC}\right)$$

Note that this is, as it should be, the same as the original equation we started with:

$$\boxed{E_0 + vt = E = iR + \frac{q}{C}}$$

One correlates the current with two variables, time (t) and charge passed (q). The charge can be measured by continuous integration of the current over time or with a coulometer in series with the ammeter measuring current.

$$i = -\left(\frac{1}{RC}\right)q + \frac{v}{R}t + \frac{E_0}{R}$$

Use the technique of multiple variable linear regression through matrix operations (linear algebra).

$$[A] = [D][k] + [\varepsilon]$$

$A$  = observation vector,  $D$  = Design Matrix,  $k$  = Parameter Vector,  $\varepsilon$  = Error Vector

$$\begin{bmatrix} i_1 \\ \vdots \\ i_n \end{bmatrix} = \begin{bmatrix} q_1 & t_1 & 1 \\ \vdots & \vdots & \vdots \\ q_n & t_n & 1 \end{bmatrix} \begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ \vdots \\ \varepsilon_n \end{bmatrix} \quad \begin{array}{l} i = \text{current} \\ q = \text{charge} \\ t = \text{time} \end{array} \quad \begin{array}{l} k = \text{parameter} \\ \varepsilon = \text{error} \end{array}$$

$$[nx1] = [nx3][3x1] + [nx1] \quad \text{for } n \text{ data points of } i \text{ in observation vector}$$

$$[3x1] = \begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix}$$

$$[A] = [D][k] + [\varepsilon] \quad [A] - [D][k] = [\varepsilon] \quad [D]^T([A] - [D][k]) = [0]$$

$$[D]^T[A] = [D]^T[D][k] \quad [k] = ([D]^T[D])^{-1}[D]^T[A]$$

$$\begin{bmatrix} k_1 \\ k_2 \\ k_3 \end{bmatrix} = \begin{array}{l} -1/RC \\ v/R \\ E_0/R \end{array}$$

The values of  $k_2$  and  $k_3$  ( $v$  &  $E_0$  known) give separate determinations of  $R$  which can then be used with  $k_1$  to determine  $C$ .

### **Capacitance:**

The primary use of electrode combined resistance and capacitance measurement is to obtain a value for electrode surface capacitance. This capacitance value can be related to the structure of the double layer at the electrode's surface. Note that electrode surface capacitance is not constant over wide ranges of applied potential. Electrode surface capacitance may be regarded as almost constant within limited ranges of applied potential. For ideal parallel plate capacitors, the following relationship exists:

$$C = \text{capacitance} = \frac{q}{E_C} = \varepsilon \frac{A}{d}$$

$\varepsilon$  = permittivity of material between plates

$A$  = area of plates

$d$  = distance between plates

$$\varepsilon = \varepsilon_R \varepsilon_0 = (\text{relative permittivity})(8.854 \times 10^{-12} \text{ F/m})$$

$$\varepsilon_0 = \text{permittivity of a vacuum} = 8.854 \times 10^{-12} \text{ F/m}$$

A non-constant differential capacitance can be defined as:

$$C_d = \text{differential capacitance} = \frac{dq}{d\psi} \quad \begin{array}{l} dq = \text{change in excess charge} \\ d\psi = \text{change in potential at electrode surface} \end{array}$$

The units of permittivity are farad/meter (F/m). A polarized electrode (*i.e.*, an electrode wherein the surface potential difference is due to the formation of a capacitor between the electrodes surface and the adjacent electrolyte with no faradaic current flowing) will develop a structure known as an electrode double layer.

At high relative capacitance, the structure of the electrode double layer will entail an excess of electric charge (either positive or negative depending on the applied potential) at the electrode's surface coupled with an excess of complementary ionic electric charge (negative or positive depending on the electrode's excess charge) in a solution zone very near to the electrode's surface both separated by a monolayer of solvent molecules adsorbed physically to the electrode's surface. The potential difference at a polarized electrode's surface changes rapidly from the value within the bulk electrode to the value in the bulk of the electrolyte. The majority of the voltage change occurs over a short distance equal to the length of the inner Helmholtz zone of electrode double layer. The rapid change in potential over so small a distance leads to very high electric field ( $\approx 5$  million volts per mm easily obtainable). At high electric field strength, the permittivity of the solvent layer adsorbed to the electrode's surface can differ significantly from the zero-field value. That is, electrode double layers are not ideal dielectrics.

If we assume that a monolayer of water molecules composes the dielectric layer, then the width of the double layer dielectric is about 0.3 nm (approximate diameter of a water molecule). Under conditions where no faradaic current is flowing and where changes in surface potential difference are limited, the differential capacitance per unit area (area specific capacitance) can be regarded as an approximately constant capacitance. The relative permittivity of water at the high electric field strength of a strongly polarized electrode is  $\approx 6$ .

$$\frac{C_d}{A} = \frac{C}{A} = \frac{\epsilon}{\delta} = \frac{6 \times (8.854 \times 10^{-14} \text{ F/cm})}{(3 \times 10^{-8} \text{ cm})} \approx 18 \frac{\mu\text{F}}{\text{cm}^2}$$

$A = \text{area}$   
 $\epsilon = \text{real permittivity}$   
 $\delta = \text{length of dielectric}$

Electrode capacitance values have been used to deduce that the dielectric present at the surface of a strongly polarized electrode is a molecular monolayer of solvent. Electrode capacitance values can also be used to deduce the change in the relative permeability of a solvent at the very high electric field strength present at the surface of a highly polarized electrode.