6A_NanoCarbon: SuperCapacitors

Electrical Engineering of Capacitor

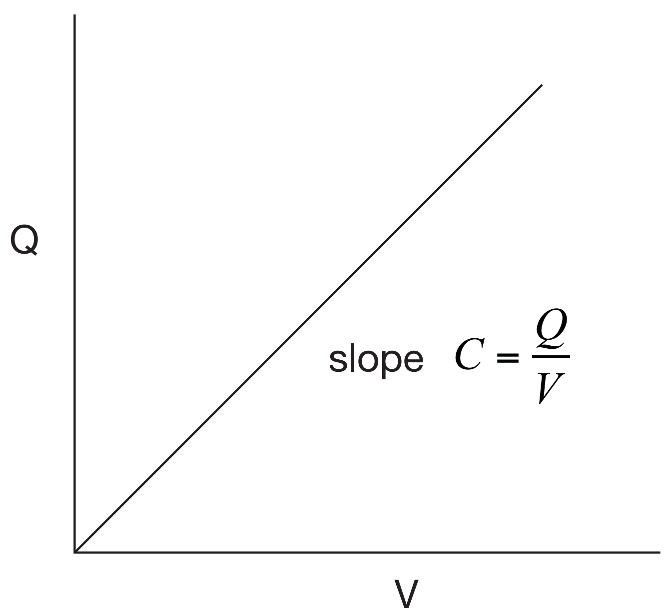
The capacitor consists of two parallel plates of a metal, separated by a distance d. The capacitance is given by

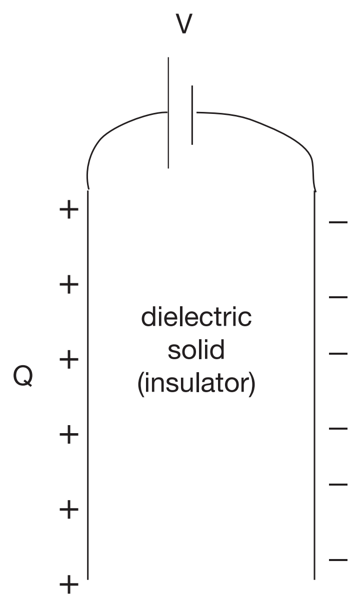
$$C = \frac{\varepsilon_r \varepsilon_o A}{d}$$

C has units of Farads

$\frac{A}{d}$ has units of m

Therefore ε_o has units of F m^{-1}

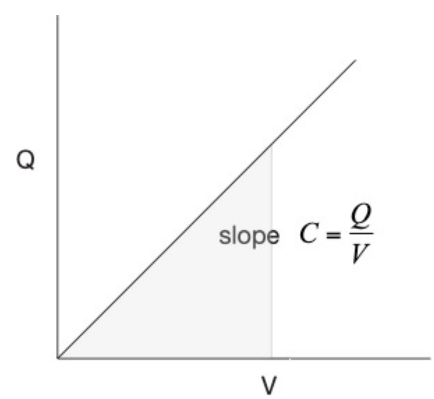




Energy stored in the capacitor

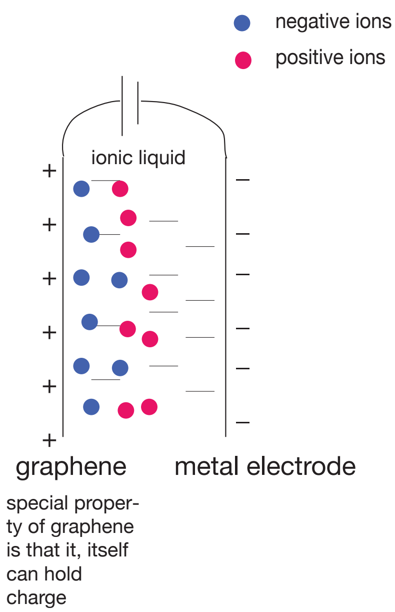
$$U = \frac{1}{2}CV^2 = \frac{1}{2}QV$$

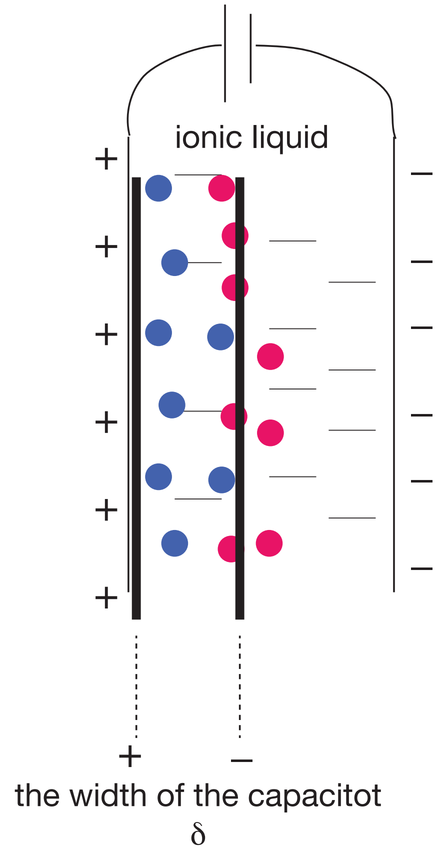
The stored energy is the area within the triangle, because the capacitor is charged gradually by increasing the voltage $dU = QdV$; $U = \int Q\,dV = \int CV\,dV = \frac{1}{2}CV^2$



The Double Layer Capacitor

Let us now consider the supercapacitor





Consider the energy of this local capacitor created by δ_D called the Debye layer. The energy stored in the electrolytic capacitor

$$U = \frac{1}{2}CV^2 = \frac{1}{2}\frac{\varepsilon_r \varepsilon_o A}{\delta_D}V^2 \qquad (1)$$

δ_D, the Debye layer is of the order of nanometers, say 5 nm. Therefore the stored energy is huge.

What about A; we wish to express the energy as density, that is energy per g. Rewriting above so that

$U \rightarrow U^*$(energy per g)
A $\rightarrow$ surface area per g

U^* is now the energy density, and A is now written as the surface area per g (SSA specific surface area).

$$U^* = \frac{1}{2}\frac{\varepsilon_r \varepsilon_o SSA}{\delta_D}V^2 \qquad (1)$$

SSA for graphene can be calculated from geometry that is the length of the bonds in the hexagonal structure, the number of carbon atoms per hexagon, and the weight of those carbon atoms (calculated from the molecular weight and the Avogadro's number)..

Calculation of δ_D

The width of the Double Layer depends on the concentration of positive and negative charges in the ionic liquid, and isgiven by

$$\delta_D = \sqrt{\frac{\varepsilon_r \varepsilon_o k_B T}{e^2 \sum_i Z_i^2 n_i^\infty}}$$

Here $k_B T$ have the usual meaning, e is the charge on an electron (1.6*10^{-19} C), and Z_i and n_i^∞ are the charge number (example Li is one and oxygen is two) and the overall concentration (number per m^3) of all the charged species (in the figures we have shown just two - red and blue) in the ionic liquid. Note that if $k_B T$ is written as RT then n_i^∞ changes into the molar concentration that is the number of moles per unit volume.

Let us insert numbers in the above equation considering a 0.01M solution of $CaCl_2$ in water.

For water $\varepsilon_r = 80$

$\varepsilon_o = 8.85x10^{-12} Fm^{-1}$

$k_B T = 1.38*10^{-23}*298\,J$

$e = 1.6*10^{-19}\,C$

$Z_{Cl} = 1$

$Z_{Ca} = 2$

Now, the concentration of the ions in water is calculated as follows. 1M means one mole in one liter of water. Therefore 1 M is equivalent to 1000M of the electrolyte in 1 m^3 of water. Therefore 0.01M means 10M of $CaCl_2$ in one m^3 of water. Now the concentration of Cl^- ions will be twice the concentration of Ca^{++} ions, as follows

$n_{Ca^{++}} = 10 N_A$ m^{-3}

and, $n_{Cl^-} = 20 N_A$, where N_A the Avogadro's number is equal to 6.023*10^{23} per mol.

Substituting the above values in the equation gives:

$\delta_D = 1.78$ nm.

Calculation of SSA for graphene

SSA has units of m^2g^{-1}. The structure of graphene consists of hexagons with a side dimension of 0.142 nm. Each carbon atom at the corners of the hexagon is shared by three hexagons. Therefore, each hexagon is occupied by two carbon atoms. Therefore ,the SSA for graphene is equal to the area on one hexagon (in m^2) divided by the weight of two carbon atoms (in g), that is

$$SSA = \frac{2\sqrt{3}a^2}{2\frac{M_w}{N_A}}$$

where a is the edge length of the hexagon in m, i.e. $1.42*10^{-10}$ m. M_w = 12 g/mol. Therefore SSA for graphene is equal to 1753 m^2g^{-1}. The effective value is closer to 500 m^2g^{-1}.

The energy density in Eq. (1) when written in terms of kWh/kg, is then given by

$$U^* = \frac{\varepsilon_r \varepsilon_o}{2*3600} \frac{SSA}{\delta_D} V^2 \quad \text{kWh/kg}$$

The highest voltage that can be applied will be equal to the water splitting voltage into hydrogen and oxygen. It is 1.23 V. Polymer electrolytes on the other hand can stand a voltage of 5 V.

Substituting SSA = 500 m^2g^{-1}, V = 5 V, ε_r = 100, and $\delta_D = 5$ nm, give an energy density of 31 kWh/kg, not a bad number.

The power density of super capacitors is of course very high because as soon as a load is applied the charge in the double layer disperses and energy stored in the capacitor is delivered to the load.

Home Work Problems (for your interest)

(i) Show that the units in Eq. (1) are balanced.

(ii) Assume the time constant for the dispersal of the double layer when the capacitor is discharged is given by τ .

(iii) Extend Eq. (1), which gives the energy density into an equation for the power density.

(iv) Assume that the dispersal time is given by $6D\tau = (\beta\delta_D)^2$, where β is some multiple of δ_D for estimating the full dispersion of the double layer - perhaps 5 would be a good number.

(v) Insert a value for the diffusion coefficient in water to obtain a number for the power density.