Supercapacitors

By
Dr. Mayank Kumar

Supercapacitor
- → Ultracapacitor (UC)
- → EDLC (Electric double layer capacitor)

Characteristics of UC:-

→ Very high Capacitance { $\underbrace{47\mu F,\ 220\mu F,\ 1100\mu F,\ 2200\mu F,\ 4700\mu F)}_{3000F}$ }

→ High energy density ✓

→ low voltage ✓

→ large life cycle

→ charging/discharging rates are very high (wrt. battery)

$$C = \frac{\epsilon A}{d}$$

$$Q = C * V$$

C = capacitance

V = potential difference.

Applications of UC :-

1. Regenerative Braking :-

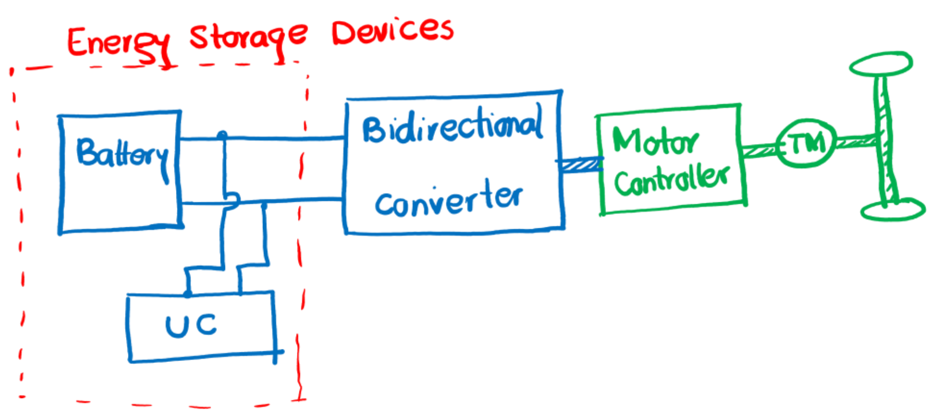
$m = 1000 kg$, $V = 36 \, Km/h = \frac{36000}{3600} = 10 m/s$

$t_{stop} = 1 \, sec$

$E = \frac{1}{2} m v^2 = \frac{1}{2} * 1000 * \overset{50}{\cancel{100}} = 50 KJ$

2. loading and unloading condition

3. start and stop of EV

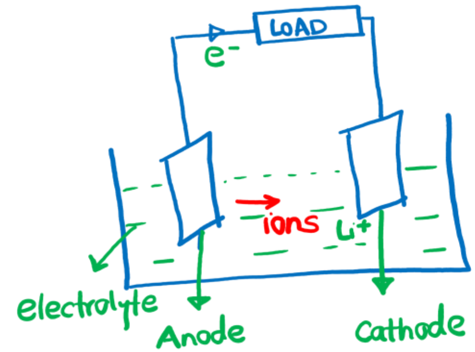


Operation of UC :-

Battery ⇨ electrochemical energy ⇒ uses ions

Capacitor ⇨ Electrical energy ⇒ uses electrons

Supercapacitor ⇨ electrical energy ⇒ uses ions



⇨ Electrolyte should have very good ionic conductivity and very poor e^- conductivity.

Lithium-ion :-

→ It is most electropositive element (3V-4V)

→ Light weight → specific power is high ≈ $0.53\ gm/cm^3$

disadvantage :-

→ reactive

→ solid electrolyte interface (SEI)

Dendritic growth inside the Li-ion :

→ Resistivity of the material ↑

→ I^2R increases (within the battery)

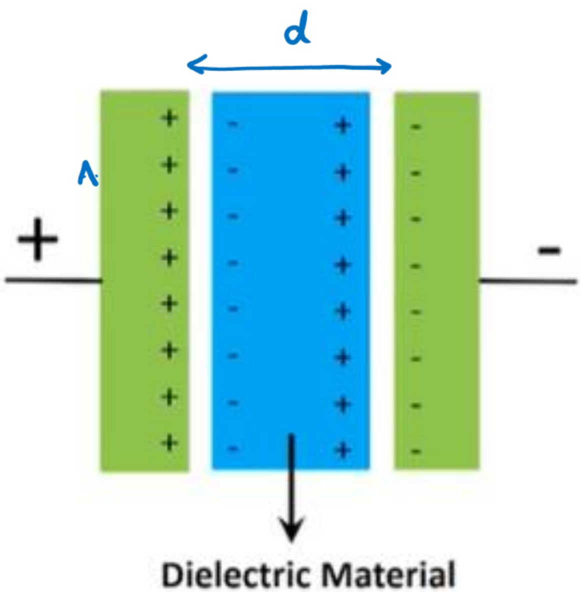
→ T ↑

} ionic conductivity ↑

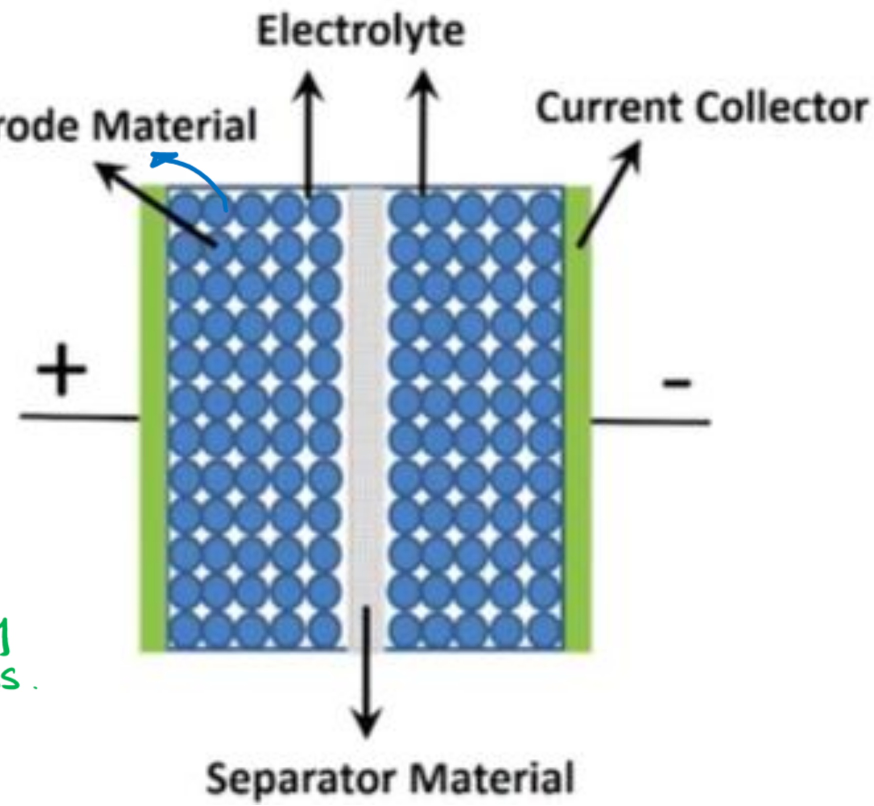
e⁻ conductivity ↓

Capacitor :-

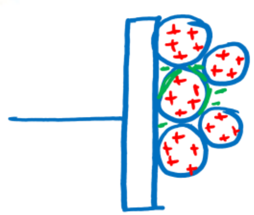
$C = \frac{\epsilon A}{d}$ ✓



Supercapacitor



electrical energy
+ uses ions.



Modeling of Supercapacitors

Basic Model

For a given application of supercapacitors, some characteristics to be considered for the design are:

- ❖ The energy that can be stored:

  Capacitance: from 1 to 3000 F

  Maximum voltage: typically 2.5 V → 2.7 V

- ❖ The energy efficiency of the charging/discharging process:

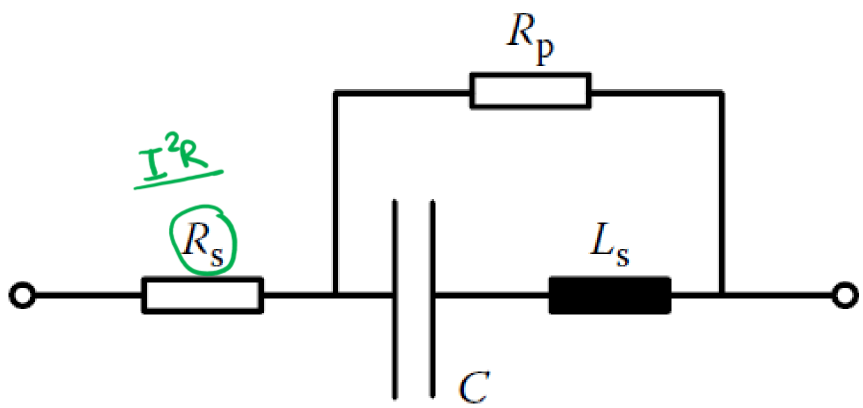
  Series resistor: limitation of the charging/discharging current

- ❖ The self-discharge:

  Leakage resistor: self-discharging of the component

Simple Equivalent Scheme

Since, the charging and discharging process is normally defined under constant current. The effect of *Ls* is then negligible.



Equivalent scheme of the supercapacitor

$R_s \rightarrow$ loss during charging and discharging

$R_p \rightarrow$ self discharge

The elements of the equivalent scheme used for modeling can be estimated through the following conditions:

- The ideal capacitor
  - Defined by the surface of electrodes
- The series resistor
  - Defined by the quality of carbon deposition on the aluminum current collectors
  - Defined by the electrical conductivity of the carbon
  - Defined by the ionic mobility of the electrolyte
- The leakage resistor
  - Overcharge beyond the decomposition limit of the electrolyte
  - Redox reaction impurities
  - Redox reaction of functional groups on the edge of carbon particles
  - Electronic conductance through the separator

Specific Behavior of Supercapacitors (Voltage-Dependent Capacitance)

- ❖ This phenomenon is related to the variation of the thickness of the double layer that appears under the action of the normal electrostatic force.
- ❖ As a consequence, the value of the capacitance increases with the capacitor voltage.

The effect of the change of the value of the capacitance can be described as follows:

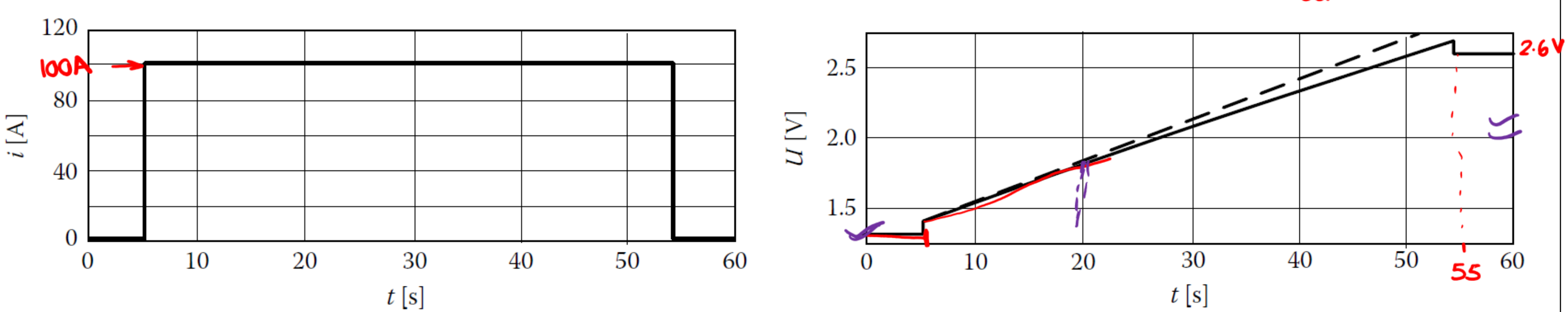
$$C = C_o + C_U = C_o + KU$$

$Q = CV$

$\frac{dQ}{dt} = C\frac{dv}{dt} + \underbrace{V\frac{dC}{dt}}_{0}$

$= C\frac{dv}{dt}$

where C_U is the voltage-dependent part of the capacitance.



Effect of the voltage-dependent capacitance.

- ❖ the voltage rate of rise is reduced when the voltage increases.

$$Q = C*V = (\underbrace{C_0}_{\text{constant}} + KV)\,V = C_0 V + K V^2$$

$$\Rightarrow \quad i_c = \frac{dQ}{dt} = C_0 \frac{dv}{dt} + \underbrace{v\frac{dC_0}{dt}}_{=0} + 2KV\frac{dv}{dt}$$

$$\boxed{i_c = \underbrace{(C_0 + 2KV)}\,\frac{dv}{dt}}$$

current capacitance $C_i = C_0 + 2KV$

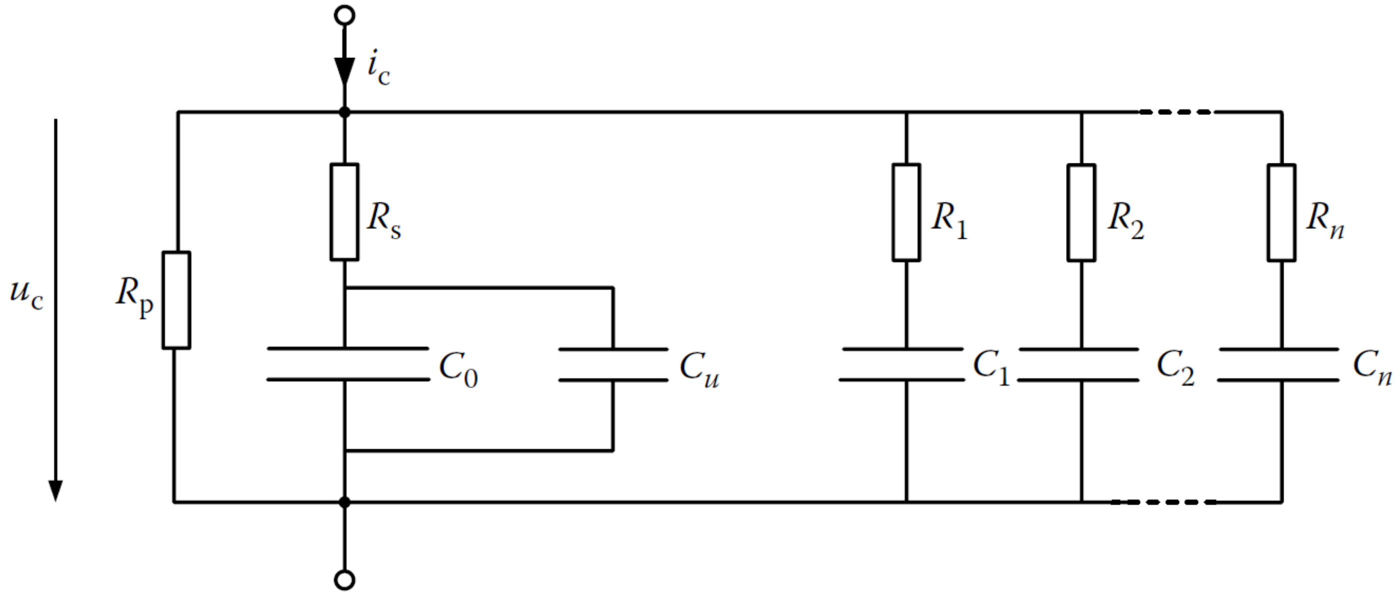
$$P = V * i_c = V\left[(C_0 + 2KV)\frac{dv}{dt}\right] = \left(C_0 V + 2KV^2\right)\frac{dv}{dt}$$

$$\Rightarrow \quad \int P*dt = \int (C_0 V\,dv + 2KV^2\,dv)$$

$$\Rightarrow \quad W_c = \int P*dt = \frac{C_0 V^2}{2} + \frac{2KV^3}{3} = \frac{1}{2}\left[C_0 V^2 + \frac{4}{3}KV^3\right]$$

$$\boxed{\text{Energetic Capacitance} = \frac{1}{2}\left[C_0 + \frac{4}{3}KV\right]V^2 = W_c}$$

Complete Equivalent Scheme



The completed equivalent scheme

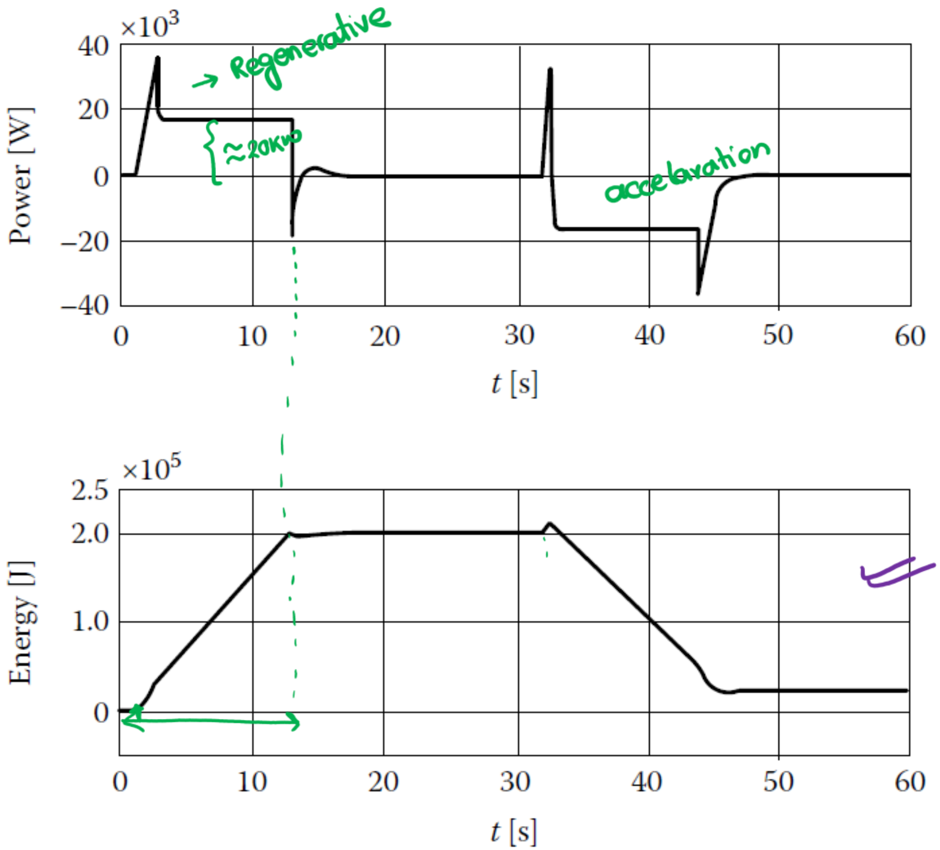
- In completed equivalent scheme of a supercapacitor, in addition to C_0, the voltage-dependent capacitance C_u is added.
- The equivalent scheme includes some additional RC circuits that represent the so-called relaxation phenomenon.

- The relaxation phenomenon is a dynamic variation of the properties of the supercapacitor due to mainly charge migration inside of the porous electrodes, i.e., misopores, mesopores, and macropores.
- During a fast charge (discharge), ions will first enter (leave) macropores and then mesopores. The diffusion of ions in misopores is characterized by longer time constants.
- During the aging process, the relaxation phenomenon is reinforced by impurities affecting the dimension of the pores.

- The diffusion of the charges for reaching a homogeneous distribution depends on the size of the pores and the size of the ions. The observable phenomena are:
  - Voltage decrease (after charge), even if the current is set to zero
  - Voltage increase (after discharge), even if the current is set to zero

Design of a Supercapacitive Bank

- The relatively low voltage of the supercapacitors gives only a limited power level and also a limited amount of stored energy.
- The example of a large element of 3000 F and 2.7 V illustrates this limitation when the energy content is around 10 kJ.



Power profile and associated energy excursion of an elevator.

$$W_c = \frac{1}{2}\underbrace{\left[C_0 + \frac{4}{3}KV\right]}_{C}V^2$$

$$= \frac{1}{2}CV^2 \qquad \left\{\text{where } C = C_0 + \frac{4}{3}KV\right\}$$

Final value of V_c at fully charged condition $= V_M$

Minimum value of V at which capacitor may discharge $= V_{min}$

$$W_U = \frac{1}{2}C\left\{V_M^2 - V_{min}^2\right\} = \text{usefull energy}$$

Discharge ratio of supercapacitor $= d = \frac{V_{min}}{V_m} * 100 \%$

$$W_U = \frac{1}{2}C * V_M^2\left\{1 - \left(\frac{V_{min}}{V_M}\right)^2\right\} = \frac{1}{2}CV_M^2\left\{1 - \frac{d^2}{100^2}\right\}$$

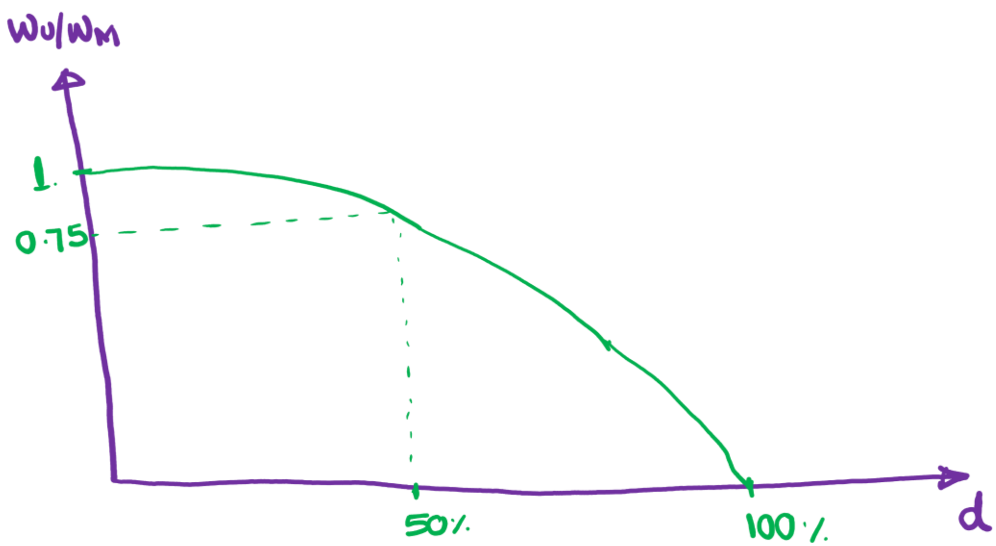
$$\boxed{W_U = W_M\left\{1 - \frac{d^2}{100^2}\right\}}$$

$$\text{No. of UC} = N_{SC} = \frac{W_R}{W_M\left(1-\frac{d^2}{100^2}\right)} = \frac{2W_R}{CV_M^2\left(1-\frac{d^2}{100^2}\right)}$$

$$W_U = W_M\left(1-\frac{d^2}{100^2}\right) \Rightarrow \frac{W_U}{W_M} = \left(1-\frac{d^2}{100^2}\right)$$

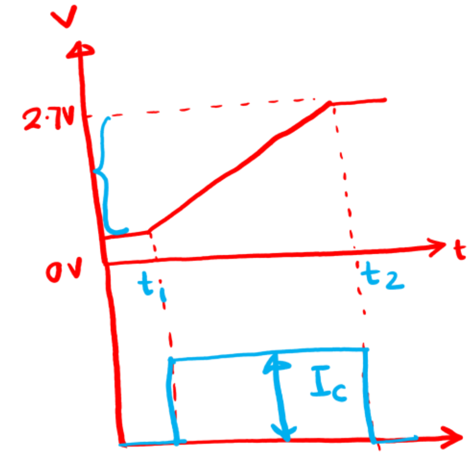
at $d = 50\%$

$$\frac{W_U}{W_M} = 0.75$$



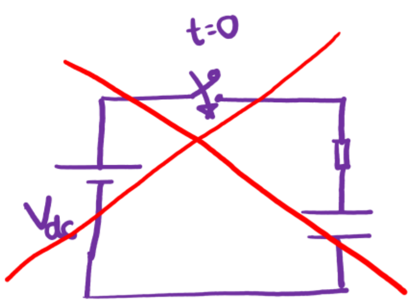
Charging and Discharging of Supercapacitor

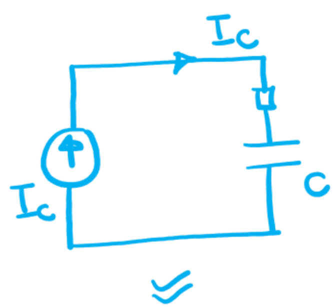
$V_c = \frac{1}{C}\int i_c dt$

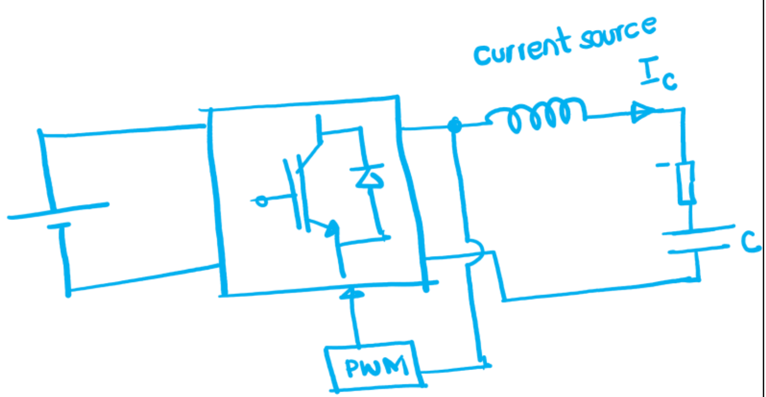


Capacitor voltage :-

$$V_c = V_{initial} + \frac{1}{C}\int_{t_{st}}^{t_{final}} I_c dt \quad — \quad (1)$$







Calculation of Charging time of SC :-

Initial state :-

$$d_i = \frac{V_{initial}}{V_M} * 100$$

Final state :-

$$d_f = \frac{V_{final}}{V_M} * 100 = \frac{V_c}{V_M} * 100 \Rightarrow V_c = \frac{d_f V_M}{100}$$

Charging of capacitor :-

$I_{cc} > 0$ and $d_f > d_i$

$$V_c = V_{initial} + \frac{1}{C}\int I_c \, dt$$

$$= \frac{d_i * V_M}{100} + \frac{1}{C} * I_c * T_{ch}$$

$$\Rightarrow T_{ch} = \left[V_c - \frac{d_i V_M}{100} \right] * \frac{C}{I_c}$$

$$\boxed{T_{ch} = \left[\frac{d_f}{100} - \frac{d_i}{100} \right] \frac{V_M * C}{I_c}}$$

Energy loss during charging :-

$$W_{LOSS} = I_{cc}^{\cancel{2}} * R_s * \frac{V_M * C}{\cancel{I}_c} \left[\frac{d_f}{100} - \frac{d_i}{100} \right]$$

$$\boxed{W_{LOSS} = I_{cc} * R_s * V_M * C \left[\frac{d_f}{100} - \frac{d_i}{100} \right]}$$

Discharging of Supercapacitor :-

$I_{cd} < 0$ and $d_f < d_i$

$$V_C = V_M \frac{d_i}{100} + \frac{1}{C} * I_{cd} * T_{dis}$$

$$T_{dis} = \frac{V_M * C}{I_{cd}} \left[\frac{d_f - d_i}{100} \right]$$

$$W_{loss}\Big|_{dis} = I_{cd}^2 * R_S * \frac{V_M * C}{I_{cd}} \left[\frac{d_f - d_i}{100} \right]$$

$$\boxed{W_{loss}\Big|_{dis} = I_{cd} * R_S * V_M * C \left[\frac{d_f - d_i}{100} \right]}$$