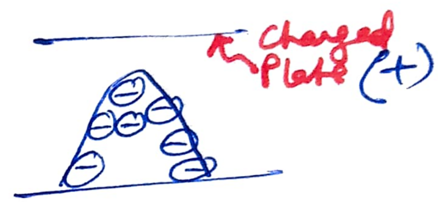
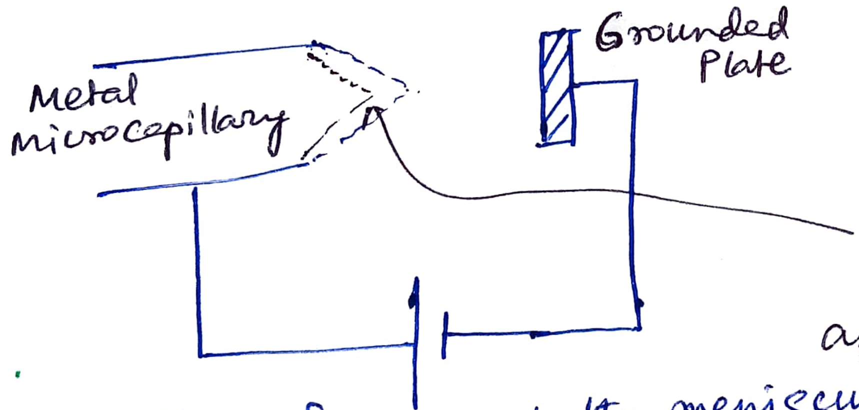
Electrohydrodynamic Atomization

* A hemispherical drop of electrolyte solution on a substrate

* Deformation into a conically shaped meniscus when a charged plate is brought close to the drop



* when the liquid is housed within a metal capillary, and a voltage is applied across the capillary and a grounded plate at a small distance away, the conical meniscus appears at the orifice.



Thin polarized layer on the liquid side of the meniscus interface forms on application of the electric field.

* Accumulation of ions at the meniscus tip leading to high charge density.
* when coulombic repulsion exceeds local surface tension, meniscus tip becomes unstable, and the charges in the meniscus are drained through extrusion of liquid jet

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Definition of Critical voltage

* Liquid meniscus protruding from the orifice in the shape of a spherical cap $\Rightarrow$ Stress arising from surface tension $= \frac{\sigma}{R}$

  where $R \equiv$ principal radius of curvature, which is of same order as the radius of capillary

* If V is the applied voltage, and d is the electrode separation, the Maxwell stress $= \epsilon_0 \epsilon_l \frac{V^2}{2d^2} = \epsilon \frac{V^2}{2d^2}$

  by which the meniscus will be pulled towards grounding plate due to coulombic attraction.

When imposed maxwell stress is greater than the stress arising from surface tension (by which the liquid meniscus held to the orifice)

$\Rightarrow$ a thin jet will be pulled out from the tip of the meniscus.

Equating the two stresses, $V_c \sim \sqrt{\frac{\sigma d^2}{\epsilon R}}$ Factor 2 is ignored.

For $\sigma \sim 10^{-2} \frac{N}{m}$

$d \sim 10^{-2}\, m$

$R \sim 10^{-3}$ to $10^{-4}\, m$

$\epsilon = \epsilon_0 \epsilon_l \sim 10^{-10} \frac{Coulomb^2}{J-m}$

$V_c \sim 10\, kV$

One volt is defined as energy consumption of one joule per electric charge of one coulomb.

Break-up of Jet

Jet that comes out from the tip of the meniscus breaks down into droplets.

Rayleigh Capillary Instability

* When charging of jet is not excessive
* Rayleigh Instability theory modified to include charge effect
* Drop diameter ~ 1.9 {Jet diameter}
* Drops are monodisperse

Coulombic Instability

* applicable for highly charged jets
* Kink instability: jet undergoes lateral whipping and bending motion
* Drops are polydisperse and significantly smaller in size.

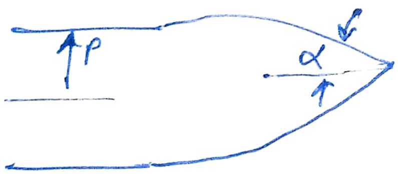
Evaporation from the drop ⇒ decrease in size
⇒ increase in charge density
⇒ Further coulombic fission and generation of finer droplets prior to deposition on grounding plate.

Spray Mode

As decided by the applied voltage and the liquid flowrate through capillary

- Continuous (a continuous jet from the tip of the capillary which disintegrates into droplets)
- Pulsating (Meniscus cone from the orifice oscillates as the droplets are ejected from the tip)

Taylor Cone :



For a perfectly conducting drop with liquid to gas permittivity ratio as ∞, cone angle approaches a limit of 49.3°.

Electrospray → DC electrospray → Concern Areas

(i) Electrolytic reactions to balance the charge, induced by applied voltage

(ii) Joule heating

(iii) Generation of other chemicals due to Faradic reaction at electrode

Electrospray → AC electrospray

The above problems could be circumvented.

Electrospinning

The electrospray jet emanating from the tip of conical meniscus solidifies due to solvent evaporation before disintegration into droplets leaves behind polymer fiber strand that can be aligned and wound by using rotating grounded electrode.

Rayleigh instability in jet
- Axisymmetric → beading in fiber
- Azimuthal → coiling, bending, winding, spiralling, looping

Random occurrence

Multiple fibers producing from single jet upon perturbation in operating parameters

Control of instability through deployment of ring electrode (grounded) around the jet, and thus creating a field around the jet.

Various timescales in electrospray process

- Hydrodynamic time scale $\sim \frac{L}{U} \sim \frac{R^2 L}{Q}$

  Residence time of the liquid in the needle

  Here, $R \equiv$ radius of liquid meniscus

  $Q \equiv$ Volumetric flowrate

  $L \equiv$ Length of the needle

- Viscous diffusion time scale $\sim \frac{R^2}{\nu} \sim \frac{R^2 \rho}{\mu}$

  Time required for meniscus to form through slide of one layer against the other.

- Charge diffusion time scale (Also referred as charge relaxation time scale) $\sim \frac{\lambda_D^2}{D_i}$

  λ_D is the Debye Length

  D_i is Ionic diffusivity

  — Time required for the ion to diffuse through distance λ_D (i.e., the distance from bulk to electrode surface).

- Elastic relaxation timescale of polymeric liquid

- For AC electrospray the time scale arising from AC frequency

Order of magnitude for different time scales

Hydrodynamic time scale $\sim 10^{-3}$ to 10^{-4} s

Viscous diffusion time scale $\sim 10^{-3}$ s

Charge diffusion time scale $\sim 10^{-5}$ to 10^{-7} s

Charge diffusion time ~~scale~~ scale is the shortest $\Rightarrow$ Sufficient time to charge the ~~[illegible]~~ polarized layer on the liquid side of the meniscus interface when the jet is moving out of the capillary.

Elastic relaxation time scale of polymeric liquid $\sim 10^{-2}$ s.

However, for AC electrospray, the additional time scale is the AC time period

$$= \frac{1}{\text{AC frequency in Hz}}$$

During AC electrospray, the polarity of the cone-jet oscillates with every half-cycle of applied frequency to produce positive and negative cone-jet.

Before the polarity reverses, the fluid must reach the tip (Hydrodynamic and viscous time scale), polarized layer must develop on the liquid side of the meniscus (Charge diffusion time scale), and elastic relaxation for polymeric liquid must have completed (Elastic relaxation time scale).

Otherwise, it would be mere elastic stretching, and/or a minor protrusion at the tip moving in and out at every polarity reversal instead of stable cone-jet formation.

$\Rightarrow$ For AC electrospray, AC time scale should be the longest.

For 50 Hz, the time scale $\sim \frac{1}{50} \sim 10^{-2}$ s

AC Electrospinning

* Fibers produced do not contain as much interfacial charge as those obtained from DC electrospinning
  ⇒ Higher diameter of the fiber (1 - 10 μm)
  ⇒ Less whipping instability
* Every half cycle in AC electrospinning at low frequency fibers ejected intermittently with each successive fiber ejected has opposite charge to its predecessor.
  ⇒ Electrostatic attraction between successive fibers
  ⇒ Individual fibers are likely to fuse into interconnected networks (this is not possible in case of DC electrospinning)
  ⇒ A monolith of interwoven fibers would be spun directly from the meniscus (POROUS MAT)
  ⇒ Potential use as scaffold for blood vessel
  " matrices for tissue engineering
  " porous membrane

AC Electrospinning ... Contd.

Critical Polymer Concentration

// Below the critical value, solidified particles form after evaporation

// Close to the critical value, both particles and fibers are formed simultaneously

Encapsulation of biomolecules

(*) In case of AC electrospinning, the entrained bulk charge neutralizes rapidly at the ground electrode

(*) The penetration depth of charge into the core of the fiber is small at high frequency AC voltage

(*) The method is ideally suited for encapsulation of proteins, DNAs, cells, organisms, and other therapeutic molecules without causing any major damage ~~due~~ of biomolecules due to penetration of charge.

Evaporation vs. polymerization/crosslinking/curing

- A fiber can solidify due to evaporation, depending on critical polymer concentration.
- A fiber can also form due to polymerization (through a focused beam of UV light, and prior addition of initiator and catalyst in the fluid)
- A fiber can form due to further crosslinking of polymer network through covalent bond formation (suitable crosslinker to be added apriori to the formulation)
- Curing of polymer fiber (completion of polymerization) through focused application of heat (by IR Lamp).

Encapsulation through electrospray / electrospinning

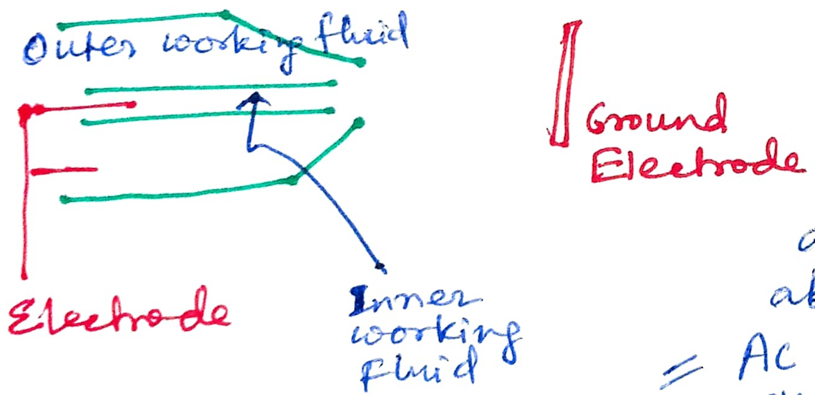
→ Blended fiber/droplet

→ Core-sheath form of fiber / capsule

Blended fiber/droplet

- First, a stable microemulsion is formed where the substance to be encapsulated (biomolecules) is the dispersed phase, and the polymer is the continuous phase
- Next, electrospray/electrospin the emulsion

Core-sheath fiber / Microcapsule



- Use of co-axial concentric annular nozzle set-up
- DC electrospinning will result in core-shell composite fiber or microcapsule depending on choice of polymer concentration above or below the critical polymer concentration.
- AC electrospinning at polymer concⁿ above the critical value will produce mat of core-shell composite fiber.

Encapsulation (Electrohydrodynamic method) .... contd.

Core-sheath fibers / Microcapsule .... contd.

/ Use of photopolymer with initiator and catalyst as encapsulating fluid that can be cured by application focused UV beam at the outlet of the nozzle — (other method of composite fiber/capsule formation apart from evaporative process)

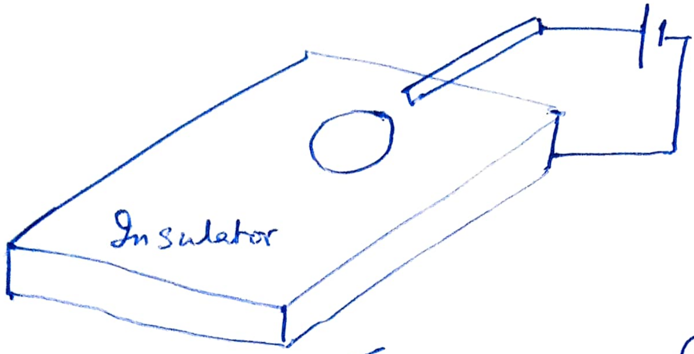
// Use of a crosslinker with the polymer, where the crosslinking process continues on the flight for fiber/capsule

≡ Use of a crosslinker bath, and collection of microcapsule through ring electrode in the bath where outer layer gets crosslinked

In case of composite fiber/capsule, both fluids need not be conducting ⇒ Insulating liquids, which cannot otherwise be electrosprayed with DC electric field can be ejected by the help of inner sheath of conducting fluid.

Because, outer insulating fluid has to form a conical meniscus as a result of viscous shear and maxwell stress imposed on the inner conducting fluid.

Discharge-driven Vortices



(*) Liquid is housed in a shallow cylindrical cavity (~ few mm depth)

(*) Sharp metal tip is raised to a voltage beyond the threshold ionization voltage of atmosphere

(*) Co-ions, repelled from the tip collides with electro-neutral air molecules, and produces bulk electrohydrodynamic air thrust, known as ionic or corona wind.

(*) When the metal tip (also referred as corona electrode) is mounted vertically above the liquid surface ⇒ interfacial deformation (slight depression will be observed

(*) When the corona electrode is inclined, the tangential component of air leads to interfacial shear, which when overcomes the viscous forces produces secondary recirculation in the bulk liquid (Microfluidic Mixing)

(*) With an AC field, permanently entrained plasma cloud is produced at each half AC cycle. Frequency must be less than a threshold value, so that the plasma gets sufficient time to diffuse away from the tip.

(*) Minimum AC voltage required is 500 V at 150 kHz. In case of DC, the voltage requirement is 2000 V.

(*) Advantages: No electrode contact ⇒ No joule heating, no electrolytic reaction and sample contamination, no penetration of charges into bulk, less destruction of biomolecules due to field penetration.