Lithium-Ion Batteries

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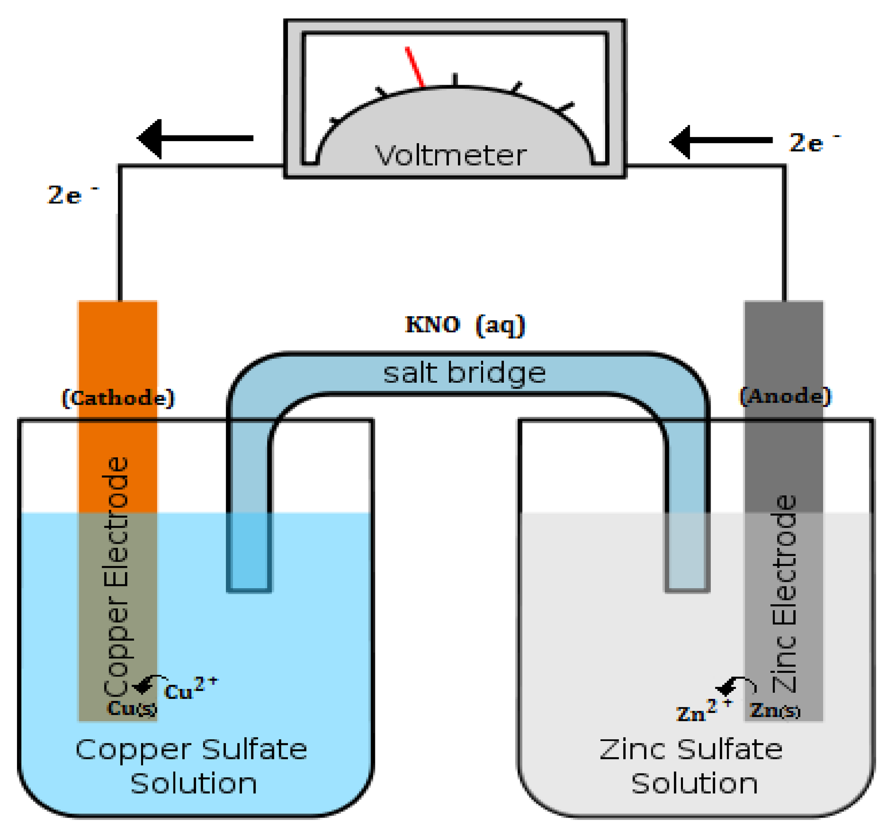
Battery Basics

- Battery components: anode, cathode, salt bridge, & electrolyte solution
- Electron flows from anode to cathode which induces electricity
- The reverse process charges the battery

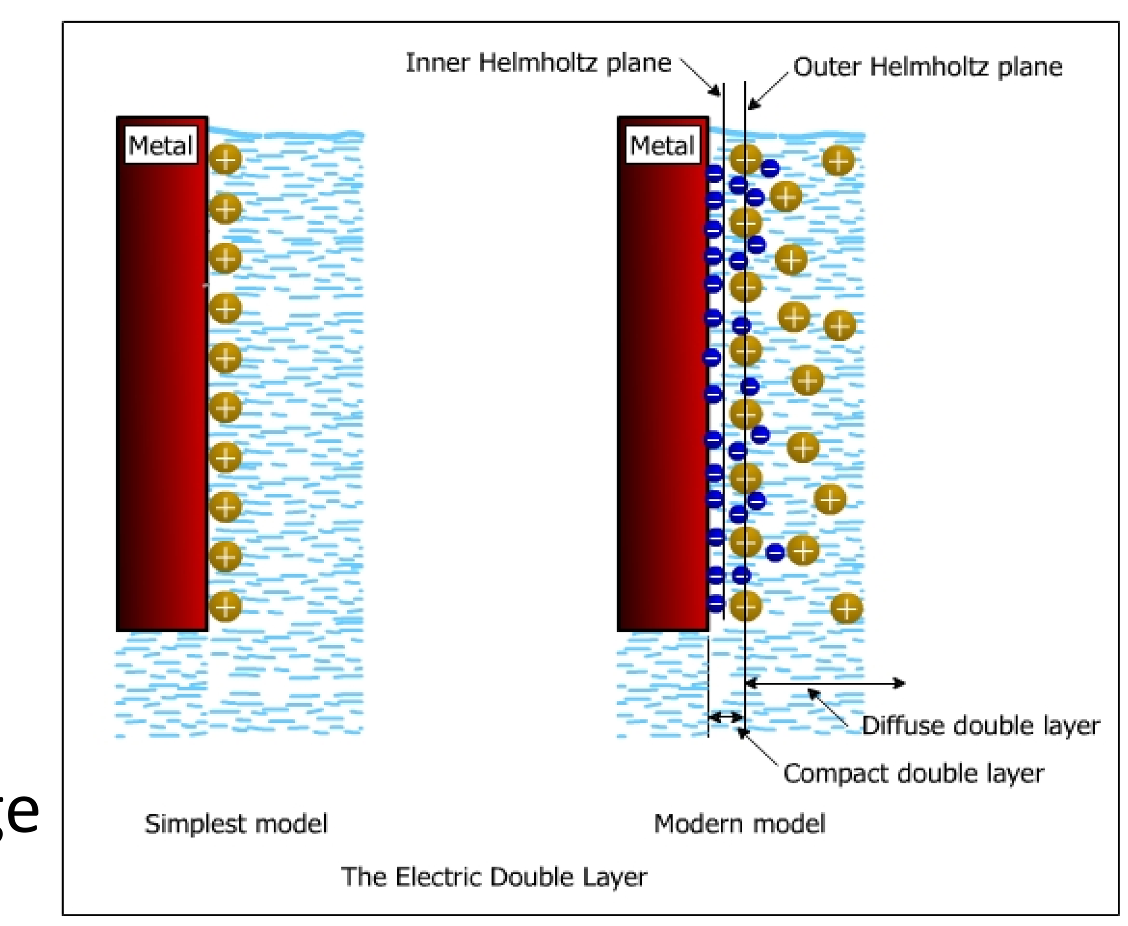


Lithium-Ion Battery Chemistry

- Anode: $LiC_6 \rightleftharpoons C_6 + Li^+ + e^-$
- Cathode: $CoO_2 + Li^+ + e^- \rightleftharpoons LiCoO_2$
- Overall: $LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2$
- Overcharging: $LiCoO_2 \longrightarrow Li^+ + CoO_2 + e^-$
- Over discharging $Li^+ + e^- + LiCoO_2 \longrightarrow Li_2O + CoO$

Electric Double Layer

- The EDL is the layer of charged particles that stack on electrodes
- There are multiple models of the EDL: Hemholtz & Guoy-Chapman model
- The relationship which describes the Hemholtz EDL: $\frac{\partial^2\varphi}{\partial x^2} = \frac{\rho(x)}{\varepsilon_1\varepsilon_0}$
- Where φ is the electric potential, x is the distance from the electrode, $\rho(x)$ is the charge density as a function of distance from the electrode, ε_0 is the permittivity of a vacuum, and ε_1 is the relative permittivity of the solution
- The density function is described by: $\rho(x) = \Sigma n_1 z_i e = \Sigma n_1^0 e z_i \exp\left(\frac{-z_i e\varphi}{kT}\right)$
- Where n_1^0 is the concentration of ion I in the bulk solution, e is the unit charge of an electron, z_i is the charge on ion I, k is the Boltzmann constant, and T is the temperature



The figure above is a model of Helmholtz and Guoy-Chapman theories respectively.

Relationships Used to Collect Data

- Poisson-Boltzmann equation (for electrostatic potentials)
- Debye-Huckel inverse shielding length $\kappa^2 \equiv \frac{4\pi e^2}{\varepsilon_m kT}\sum_j z_j^2\rho_j$
- Bjerrum Length $B_z \equiv \frac{e^2}{\varepsilon_m kT}|z_+ z_-|$
- Ionic Strength $I \equiv \frac{1}{2}\sum_j z_j^2\rho_j$

$$\nabla^2\Psi_c(r) = -\frac{4\pi}{\varepsilon_m}\sum_i z_i e\rho_i \exp[-\beta z_i e\Psi_c(r)]$$

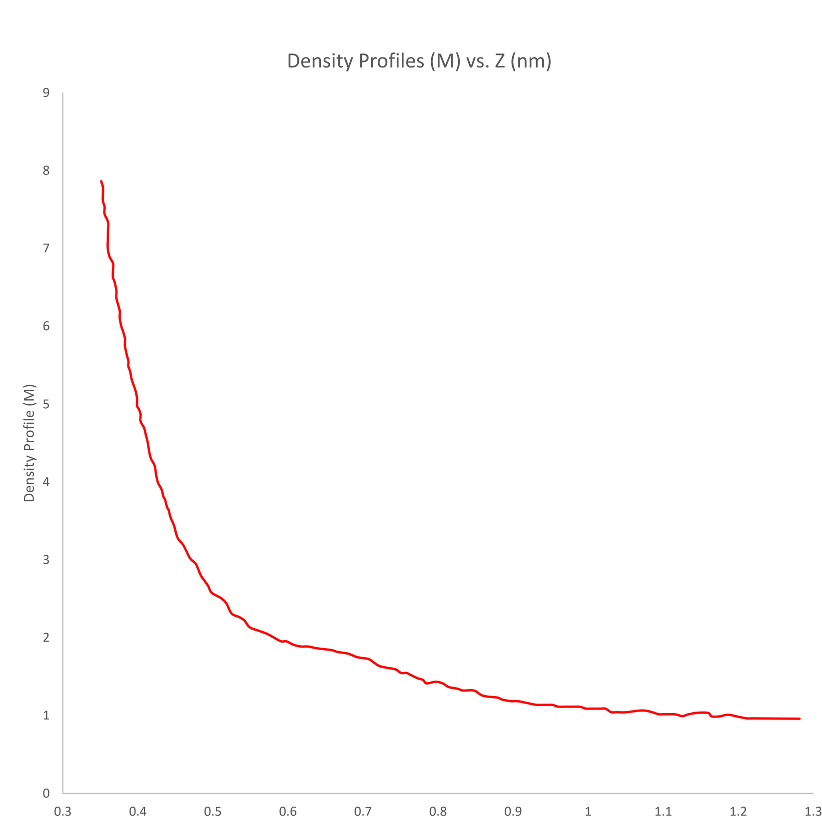
$$\nabla^2\Psi_c(r) = \kappa^2\Psi_c(r)$$

$$\kappa^2 \equiv 4\pi B\sum_j z_j^2\rho_j$$

$$\kappa^2 \equiv \frac{8\pi e^2 I}{\varepsilon_m kT} = 8\pi BI, \quad or \quad \kappa = \sqrt{8\pi B}\sqrt{I}$$

Monte-Carlo Data

- Extracted data from charts from papers and reports using Monte-Carlo method
- Web digitizer helps set bounds and extract data points from image graph
- Gives us data to work with when physical lab data is not obtainable



Fortran

- Base code to MATLAB
- Used for all calculations in project
- Quicker results than MATLAB due to large amount of iterations required
- Free software that can be found online

```fortran
!... Calculaet Debye Inverse Length kappa for NaCl Solutions
      real*4 M,k,kappa,kappa2,Ionic
      dimension M(6),d(6),c(6),rhop(6),rhom(6)
      data M/0.1,0.2,0.32,0.50,0.80,1.2/
      data d/1.000115,1.00519,1.00998,1.0708,1.02865,1.04365/

      open (15,file='kappa.txt',status='unknown')

!...            Input data
      e= 1.60206e-19          !Coulomb of unit electron
      em= 78.358*111.2e-12    !permittivity of water at 25oC.  C^2/(N.m^2)
      k= 1.38054e-23          !Boltzmann constant. J/K
      T= 298.15               !Kelvin
      zp= 1.0                 !Valence cation
      zm=-1.0                 !Valence anion
      WNaCl= 23.0+35.45
      pi= 3.1415926535

!...            Bjerrum length (1 meter= 1.0e+10 Angstroms)

      B= e*e/(em*k*T)*1.0e+10
      print *, 'Bjerrum length, B=',B,' Angstrom'

      Write(15,"('Bjerrum length:B=',g12.5,'  Angstrom')") B

!...            Calculation of Parameters
!...            Basis: 1000 g of pure water
      Do 4 i=1,6
      c(i)= M(i) *(1000.*d(i)/(  M(i)*WNaCl+1000.))   !Molarity
      rhop(i)= c(i)*6.022e-1/1000.                       !Cation number density, 1/A3
      rhom(i)= c(i)*6.022e-1/1000.                       !Anion number density, 1/A3
      Ionic= 0.5*(rhop(i)*zp**2 + rhom(i)*zm**2)         !Ionic strenth

      kappa2 = 8.*pi*B*Ionic
      kappa = sqrt(kappa2)                               !Debye kappa (1/A)

      print *,'i',i,', M=', M(i),', c=',c(i),', kappa=',kappa
      Write(15,"(i5,2x,', M=',g12.5,'kappa=',g12.5)")i,M(i),kappa

 4    continue
      print *,'=======Voila, Bon Soir======='

      stop
      end
```