Diffusion in Battery Cells

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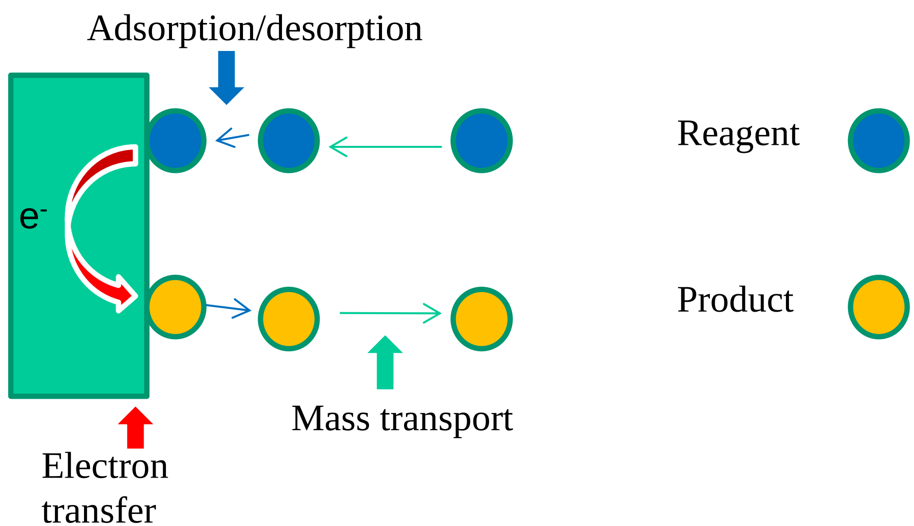
Solid redox reactions need solid diffusion

SOLUTION

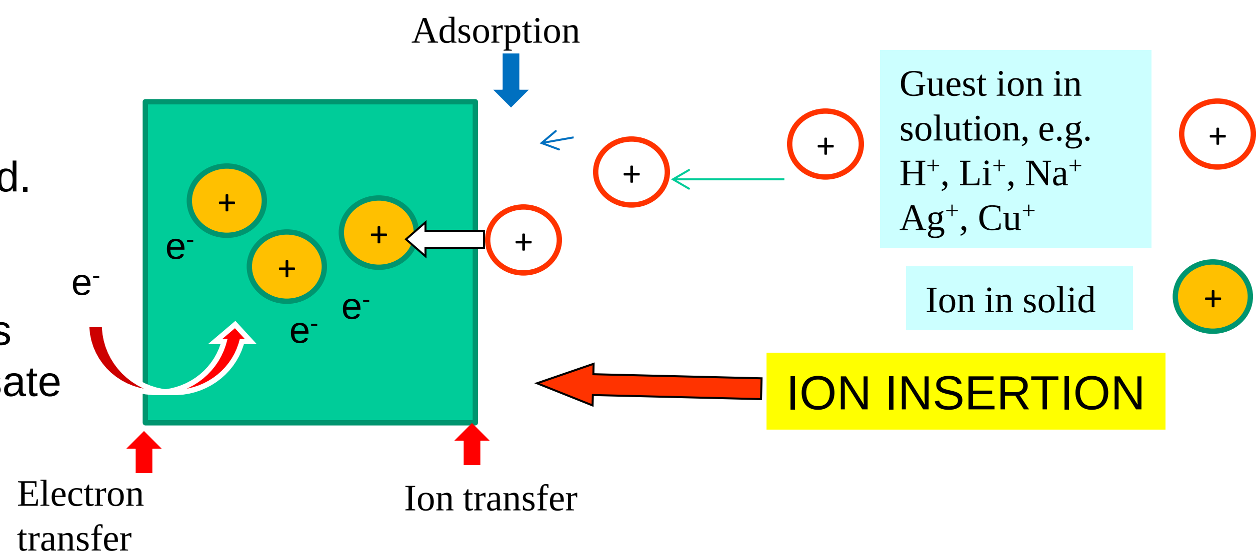
The redox reagent is initially in the solution. It diffuses to the interface, reacts, then returns to the solution,



SOLID

The reagent is a solid.

The guest ion enters the solid to compensate the charge.



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Diffusion is slow, specially in the solid state

time constant = L^2/D

Estimate the time required for lithium ions to diffuse a distance of 100 μm. Use the approximation $t=L^2/D$
and consider $D=10^{-10}$ cm^2/s

Answer: 10^6 seconds (280 hours)

Diffusion is slow, specially in the solid state

Estimate now the time required for lithium ions to diffuse a distance of 100 nm. Use the approximation $t=L^2/D$
and consider $D=10^{-10}$ cm^2/s

Answer: 1 seconds

Diffusion in Battery Cells

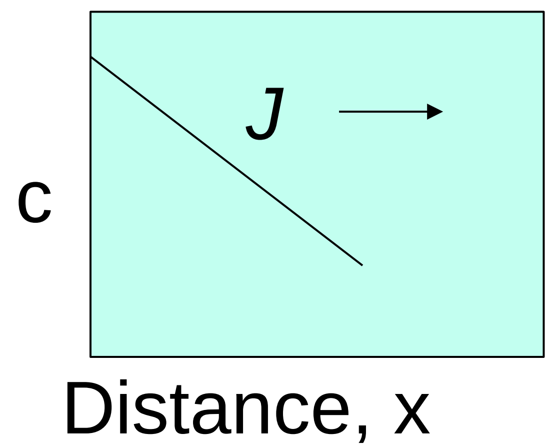
Fick's First Law:

Flux

$$J(mol\ cm^{-2}s^{-1}) = -D\frac{\partial c}{\partial x}$$

(with Faraday) Current/area

$$j\ (Acm^{-2}) = -nFD\frac{\partial c}{\partial x}$$



Diffusion in Battery Cells

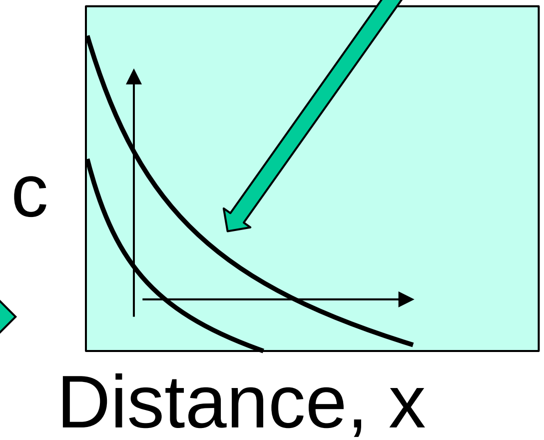
Fick's Second Law:

Positive Curvature accompanies accumulation

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

Current in:

j *(Acm* $^{-2}$) $= -nFD\frac{\partial c}{\partial x}$(x=0)

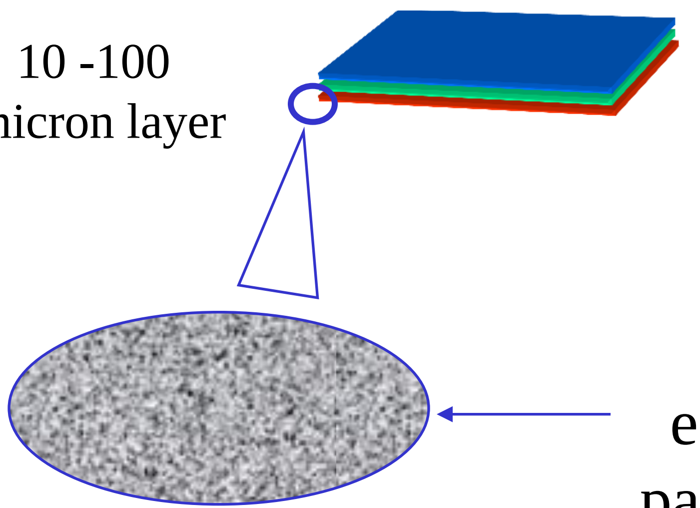


Solution: Composite Electrodes!

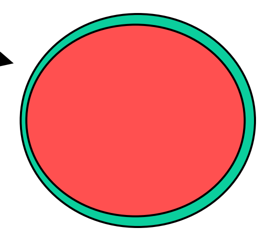
Made of active material + conductive additive (carbon) + binder

All solid state electrodes. e.g. 100 h

10 -100
micron layer



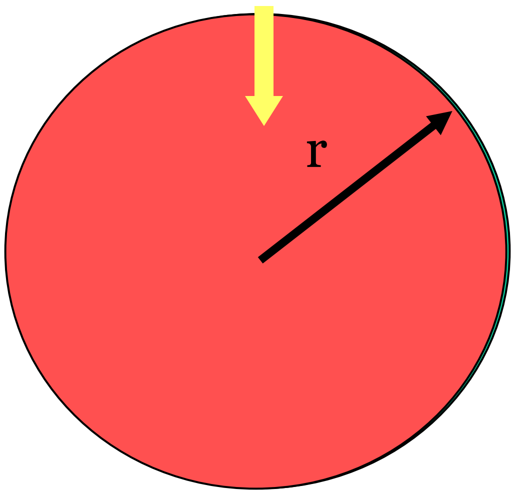
e.g. 1 micron
particles or less

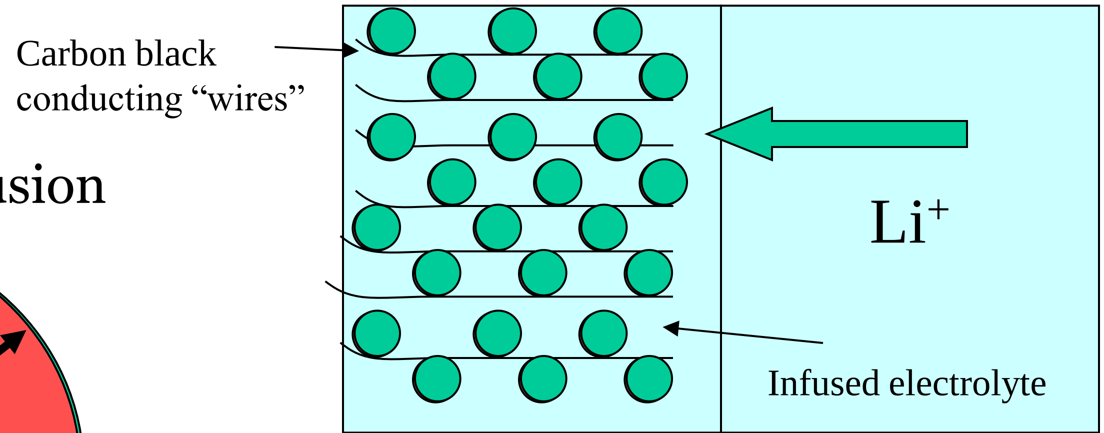


Composite electrode, < 1 h

Composite Electrodes

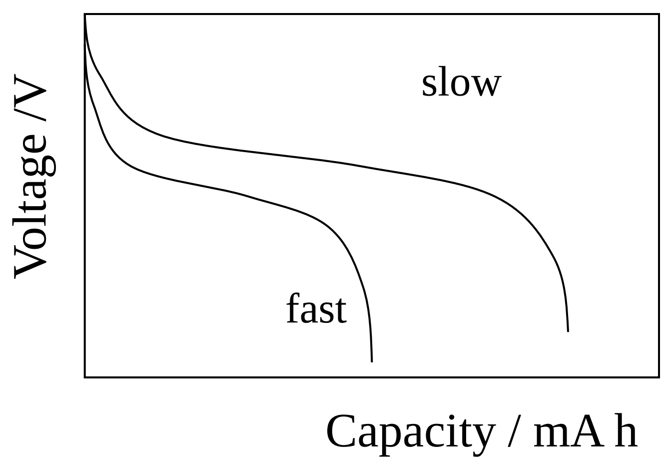
Solid state diffusion





All particles react together and concentration polarisation occurs within the particles.

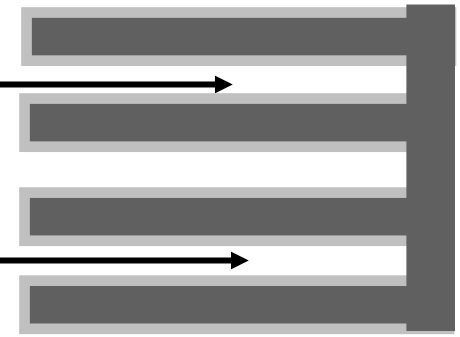
Discharge profiles:



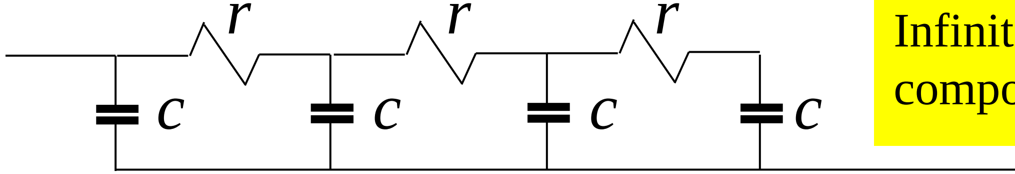
Rough and Porous Electrodes: the De Levie model

electrolyte resistance per unit electrode length, *r*

capacitance per unit electrode length, *c*



Equivalent circuit



Infinite sum of small components

Result:
Effective diffusion coefficient = r*c

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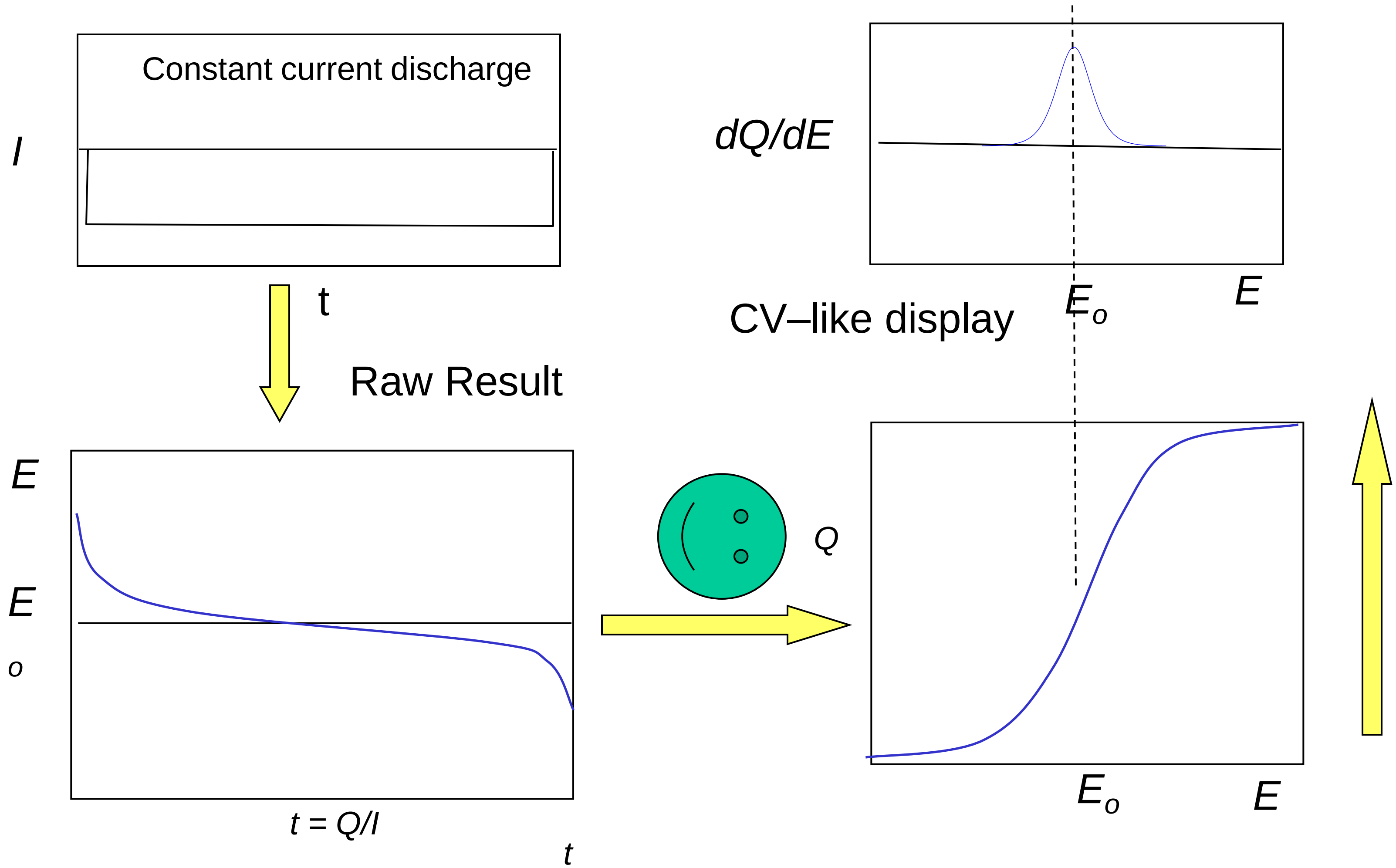
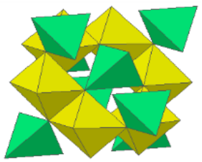
Derivative Chronopotentiometry(DCP)



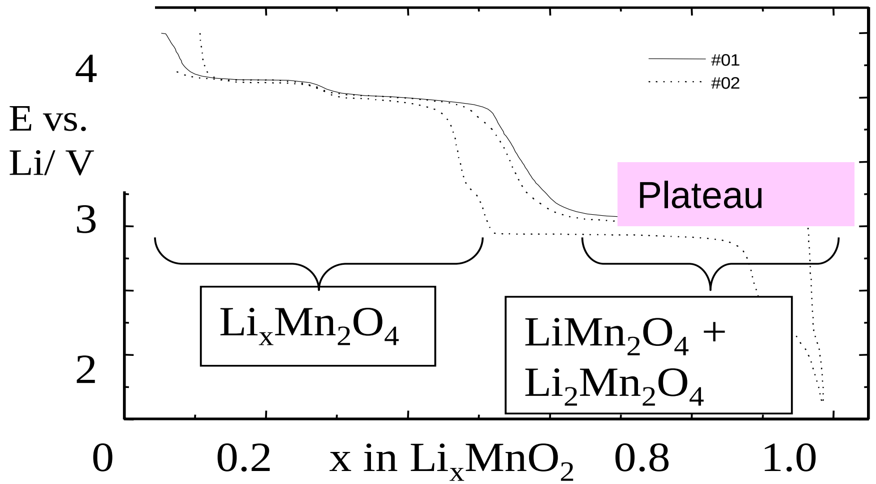
IR drop is constant - does not increase toward peak top

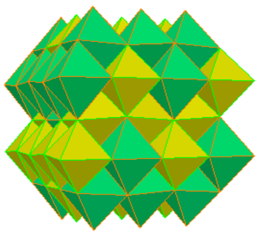
DCP for a Li-ion positive electrode

The Spinel $Li_xMn_2O_4$ lithium cathode shows both 1-phase and 2-phase insertion reactions

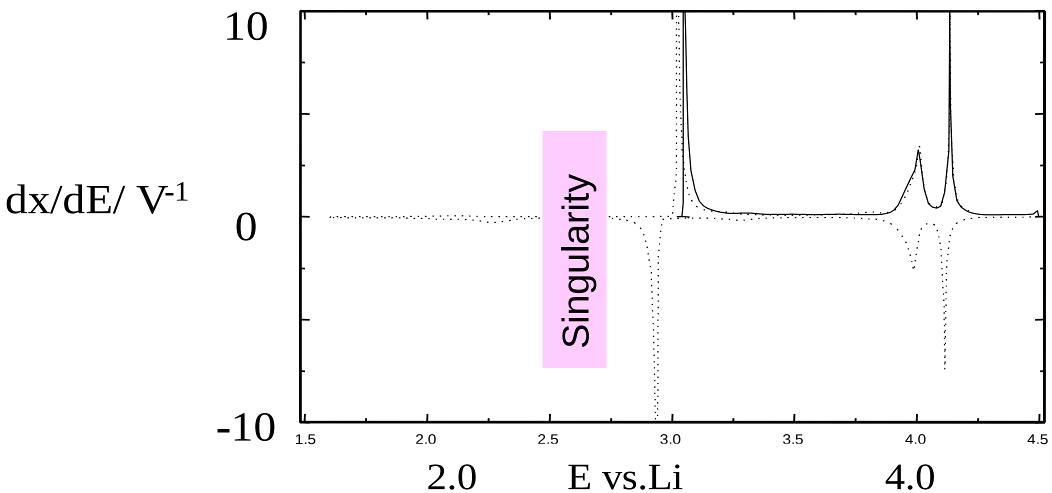


Spinel-type $Li_xMn_2O_4$





NaCl-type $Li_2Mn_2O_4$



- N.B. plateau in E gives singularity in dx/dE

- Nernst Equation gives const $E = \Delta G/nF$

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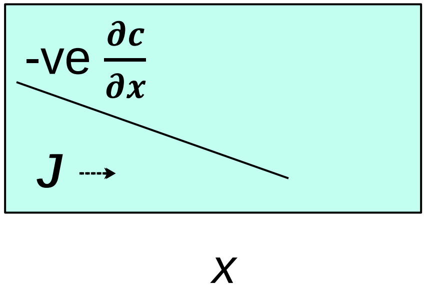
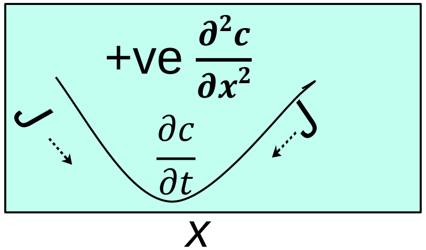
Fick's laws of Diffusion and the Sand Equation for constant current

- 1st law: flux $J_{Li+} = -\mathrm{D}\dfrac{\partial c}{\partial x}$



- 2^{nd} law: $\dfrac{\partial c}{\partial t} = -\dfrac{\partial J}{\partial x} = \mathrm{D}\dfrac{\partial^2 c}{\partial x^2}$



- Current pulse boundary conditions

  $J_{Li+}\,(x=0) = j\,/\mathrm{F}$ where j = current / area

- Result: c increases as $\boldsymbol{jt^{1/2}}/nFD^{1/2}\pi^{1/2}$

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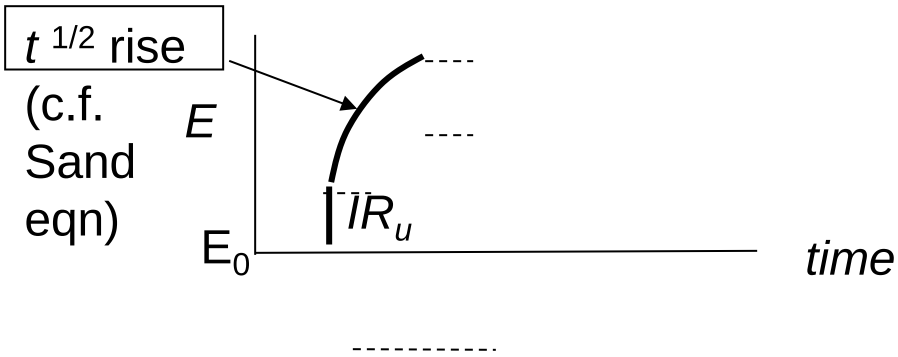
Chronopotentiometry

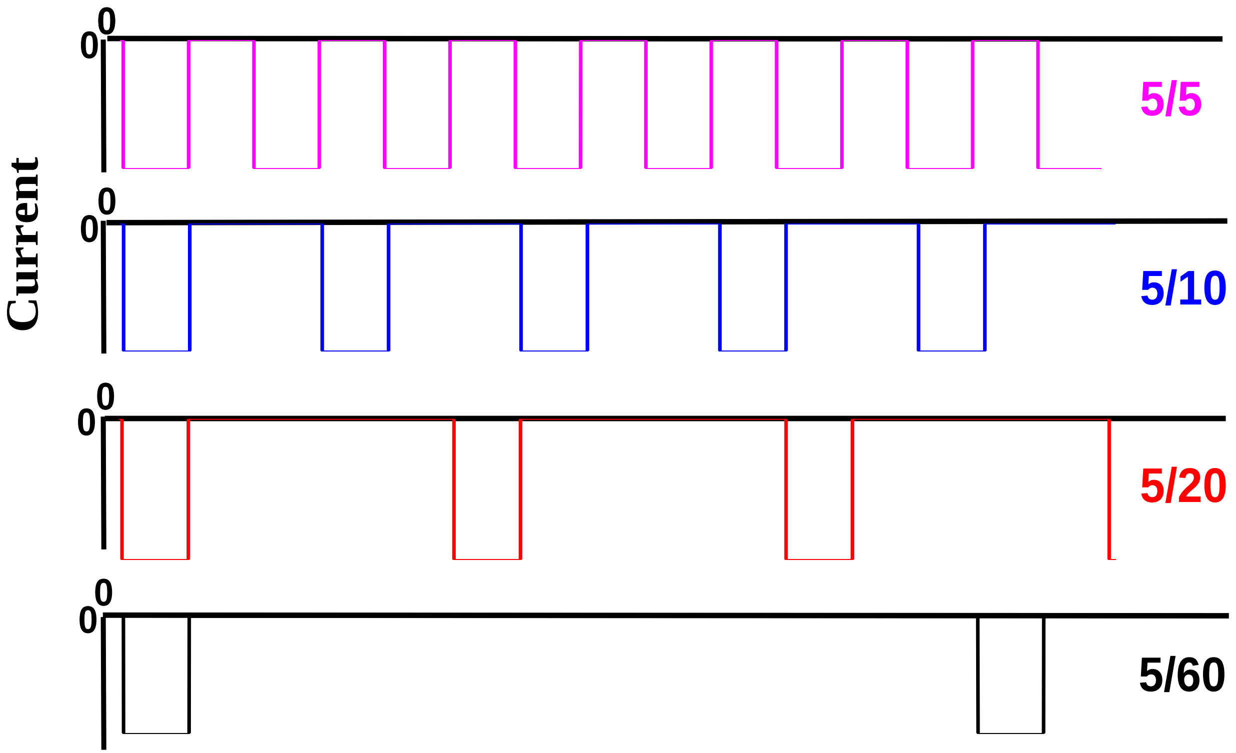
- Constant current pulse
- Measure potential vs time
- Measure equilibrium potential after the pulse



0 *L*

c increases as $\boldsymbol{jt^{1/2}}/nFD^{1/2}\pi^{1/2}$

The Galvanostatic Intermittent Titration Technique (GITT)



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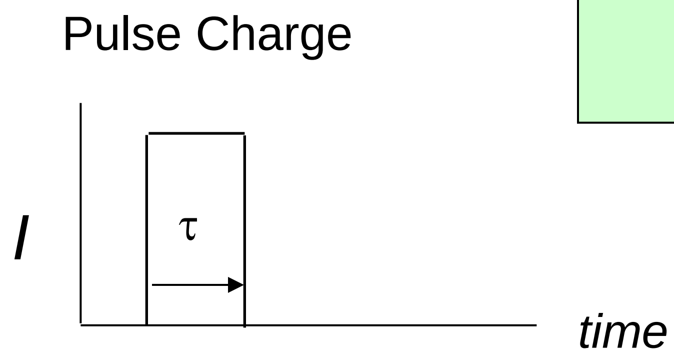
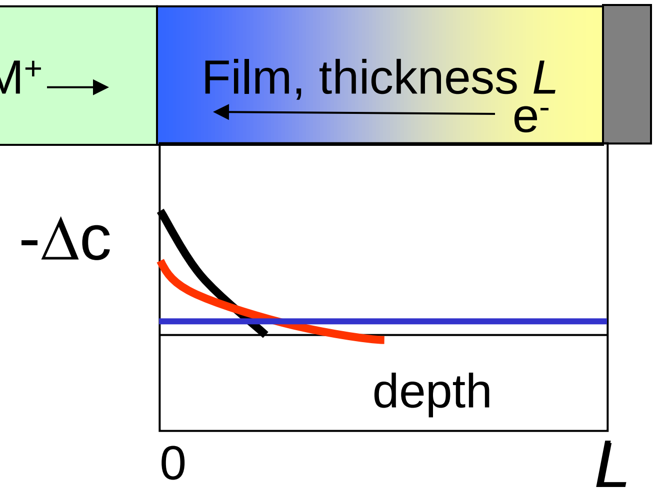
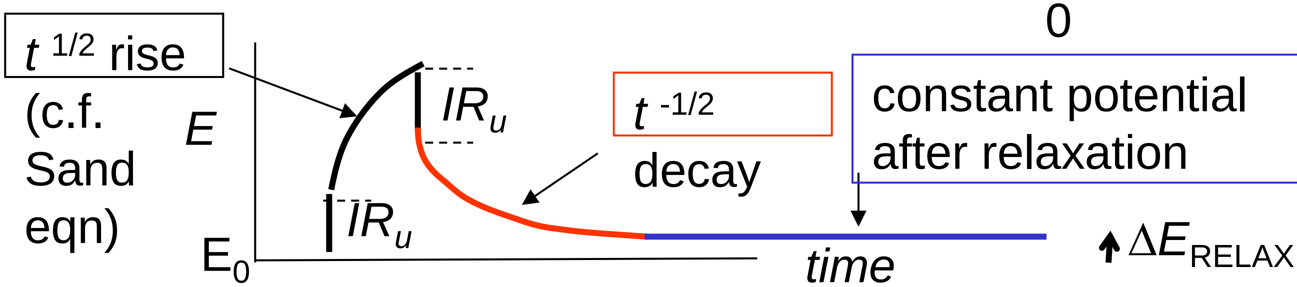
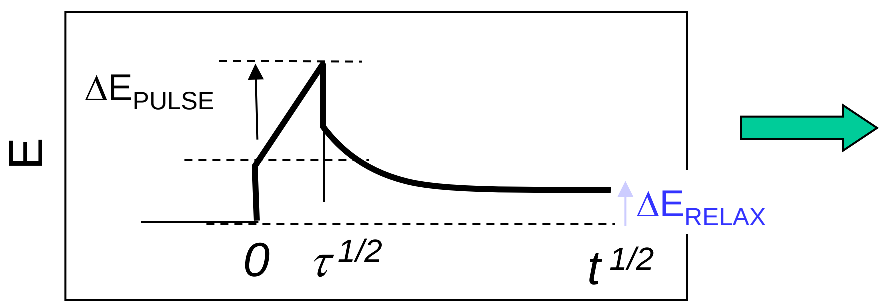
Current pulse analysis (GITT) to measure diffusion in single phase materials









$$D = \left(\frac{4}{\pi}\right)\left(\frac{L^2}{\tau}\right)\left(\frac{\Delta E_{RELAX}}{\Delta E_{PULSE}}\right)^2$$

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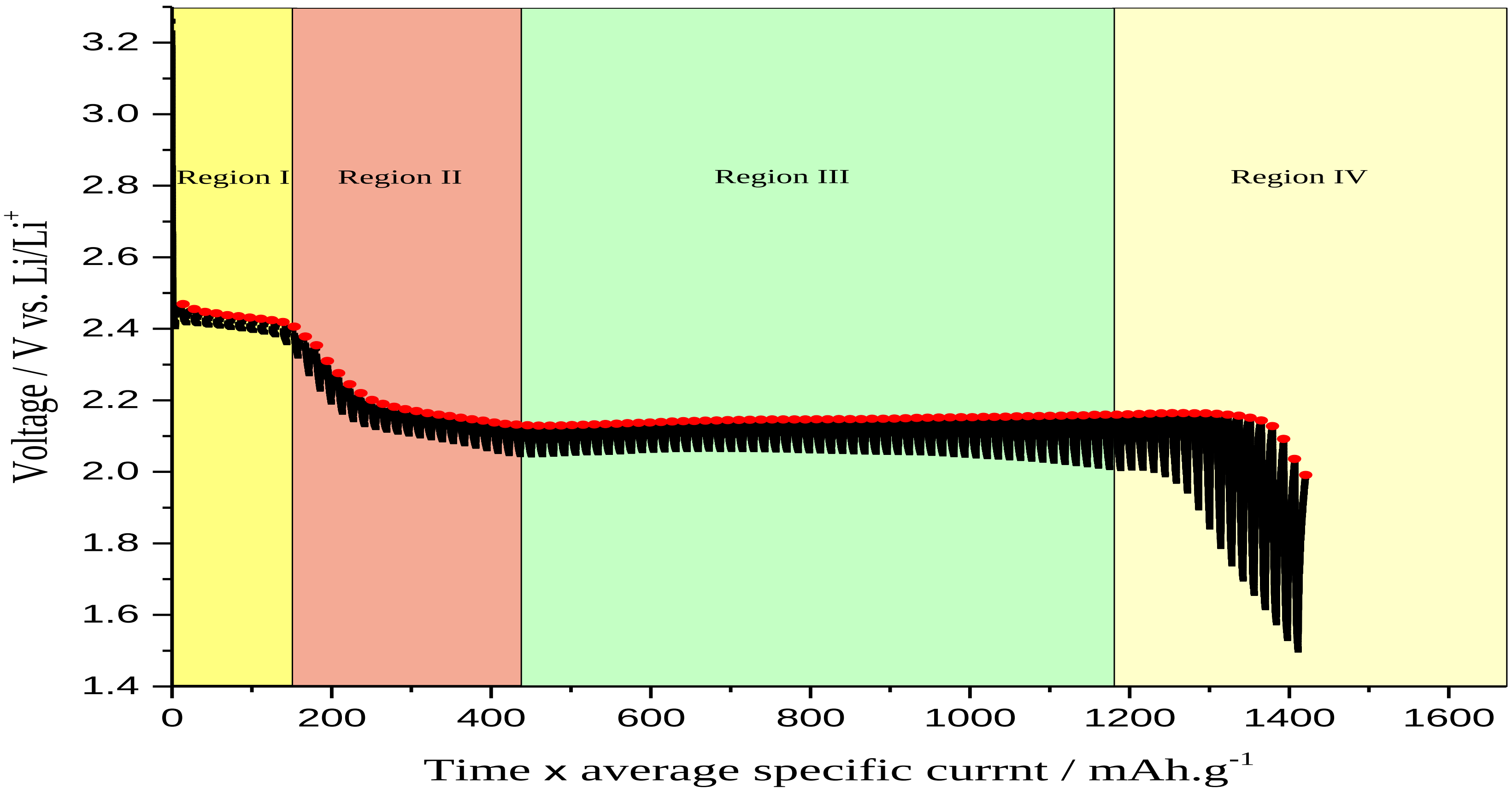
A complete titration



GITT profile for first discharge of Li/S cell using 5 min pulse and 10 min relaxation (5/10), with 1M LiTFSI in TEGDME/DOL. The red circles represent the last data point at the end of each relaxation period at discharge state of Li−S cell.

GITT also shows the thermodynamic discharge curve

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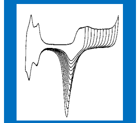
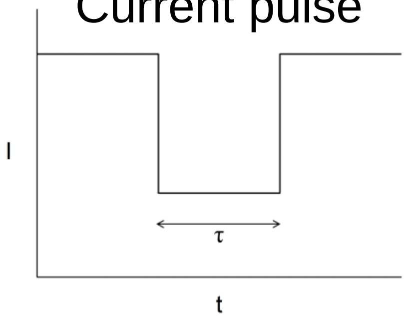
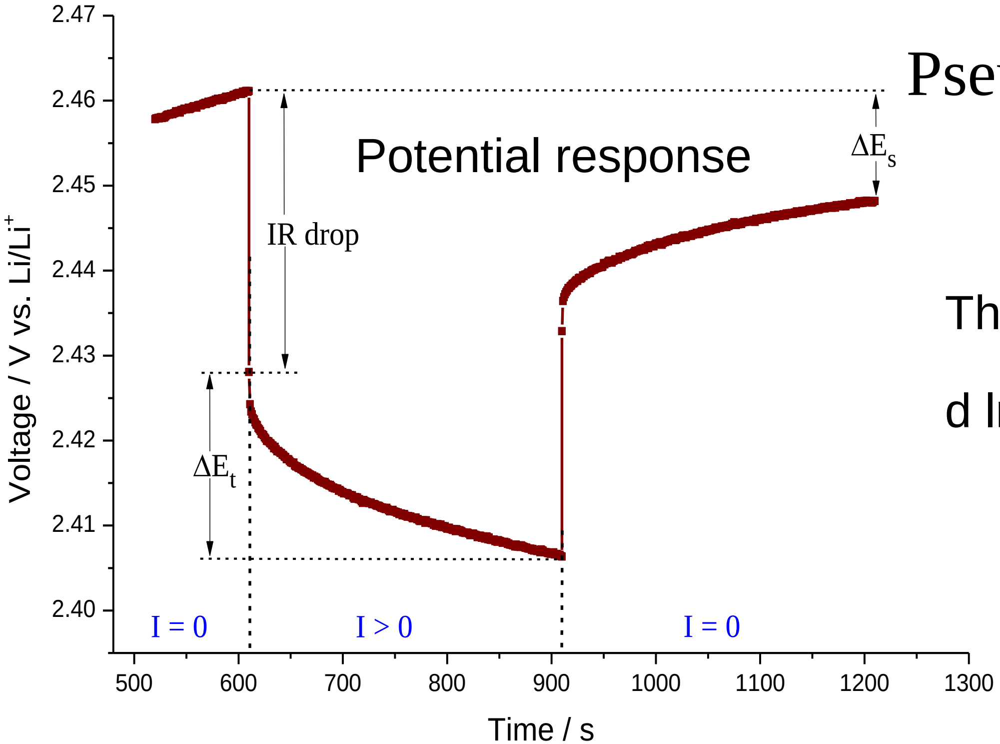


Further GITT analysis

Current pulse





$$D = \left(\frac{4}{\pi}\right)\left(\frac{L^2}{\tau_{pulse}}\right)\left(\frac{dEs}{dEt}\right)^2$$

$$\text{Pseudocapacitance, } C_v = \frac{dq_v}{dEs}$$

Thermodynamic Factor

$$d \ln a / d \ln c = \left(\frac{F^2 c}{RT}\right)\left(\frac{dE_S}{dq}\right)$$

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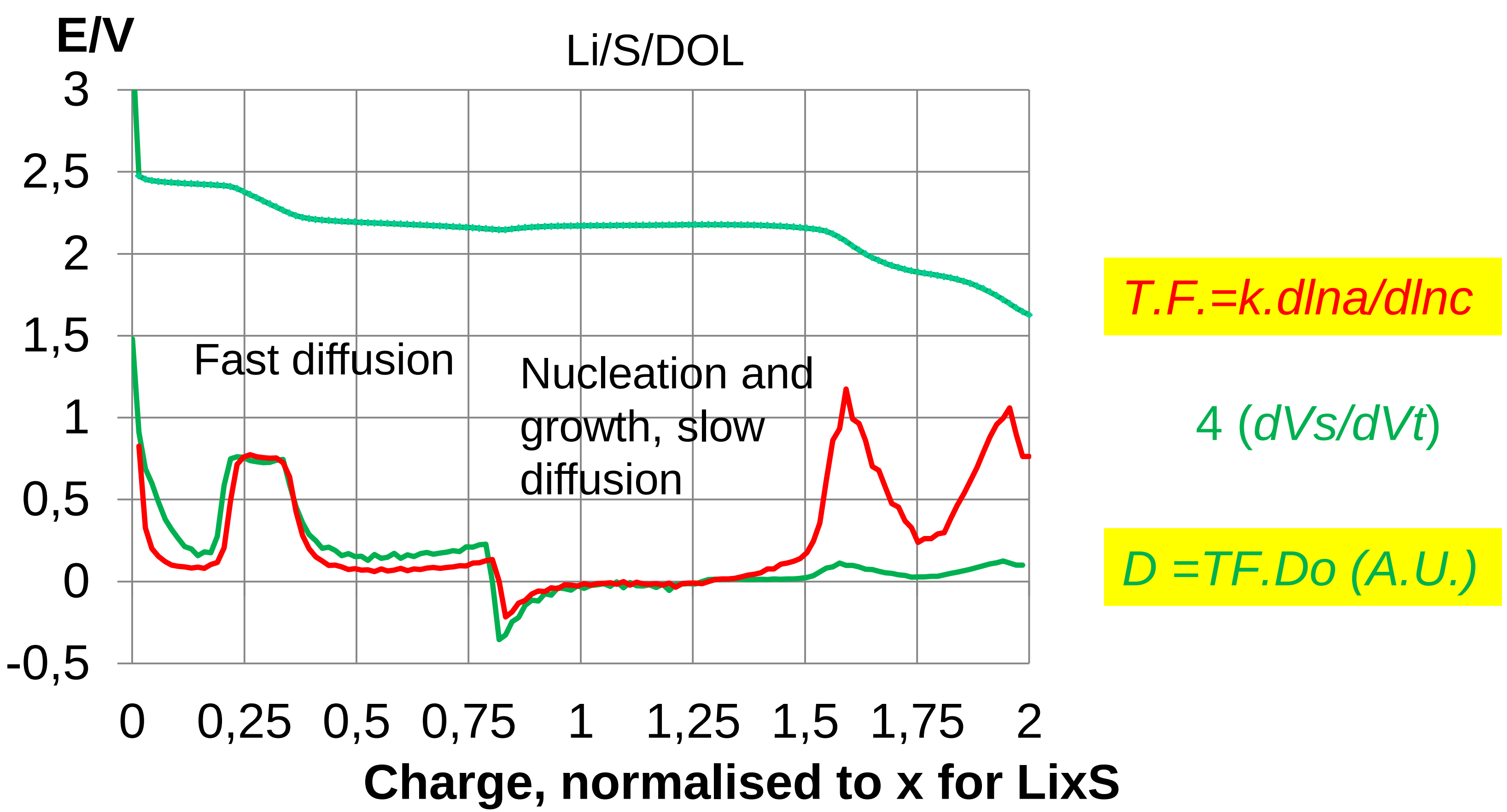
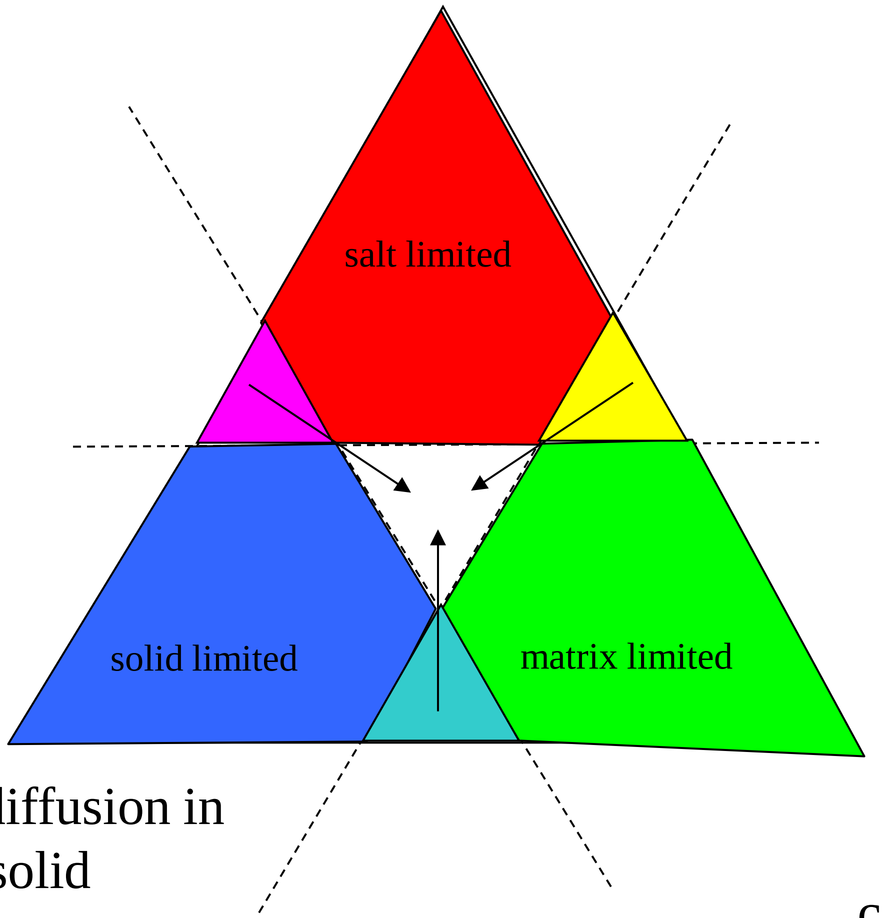
Relaxed Potential, Diffusion Coefficient, Pseudo-capacitance and Thermodynamic Factors from GITT



- *D* generally follows *T.F.* except at end point where tortuosity is high.
- Anomalous diffusion at 0.8 followed by *T.F.* = 0.
- Suggests nucleation & growth of a solid phase during which *D* value is invalid.

Conclusion – the rate limiting step rules !

Slow ion diffusion in the electrolyte



Slow ion diffusion in the solid

Slow ambipolar diffusion in the composite electrode

Summary

- Diffusion is modelled by Fick's 1st and 2nd Laws
- Slow diffusion in solds is compensated by fine particle composites
- Galvanostatic potentiometry gives $t^{1/2}$ potential profiles, measuring D at a single composition
- GITT gives both Thermodynamic and Diffusion data over a range of compositions,

Diffusion in Battery Cells

Fick's First Law:

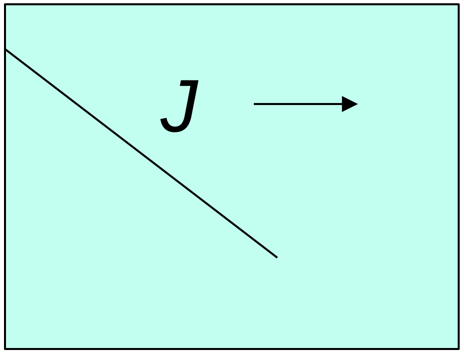
Flux

$$J(mol\ cm^{-2}s^{-1}) = -D\frac{\partial c}{\partial x}$$

(with Faraday) Current/area

$$j\ (Acm^{-2}) = -nFD\frac{\partial c}{\partial x}$$

c



Distance, x

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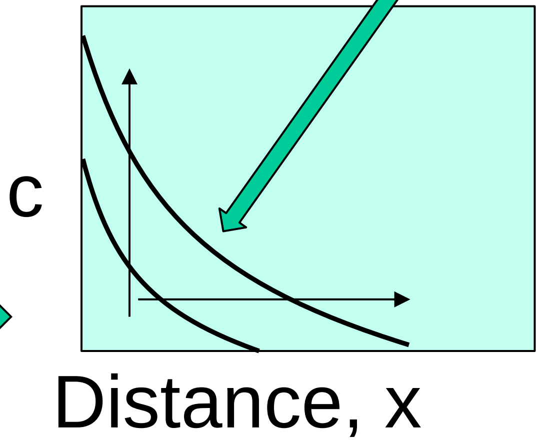
Diffusion in Battery Cells

Fick's Second Law:

Positive Curvature accompanies accumulation

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$



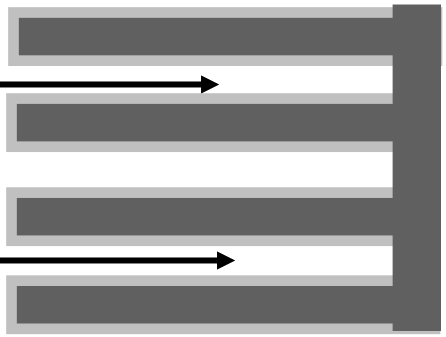
Current in:

j (*Acm* $^{-2}$) $= -nFD\,\frac{\partial c}{\partial x}$(x=0)

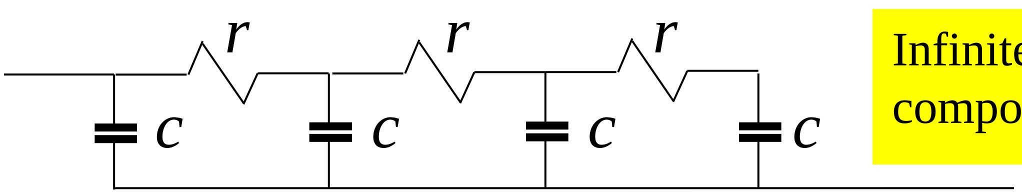
Rough and Porous Electrodes: the De Levie model

electrolyte resistance per unit electrode length, *r*

capacitance per unit electrode length, *c*



Equivalent circuit



Infinite sum of small components

Result:
Effective diffusion coefficient = r*c

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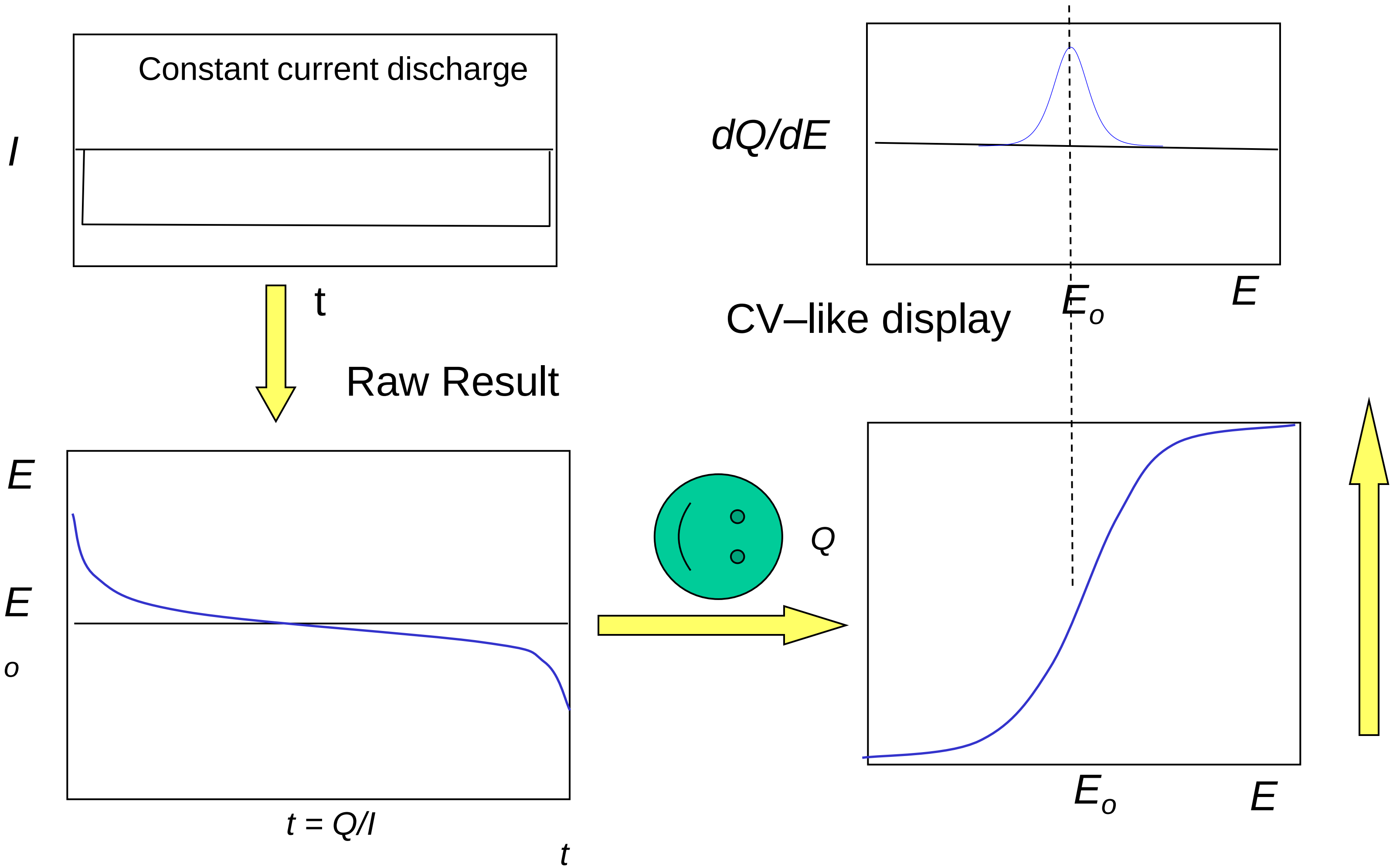
Derivative Coulometric Titration (DCT)



IR drop is constant - does not increase toward peak top

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DCT for a Li-ion positive electrode

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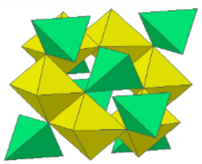
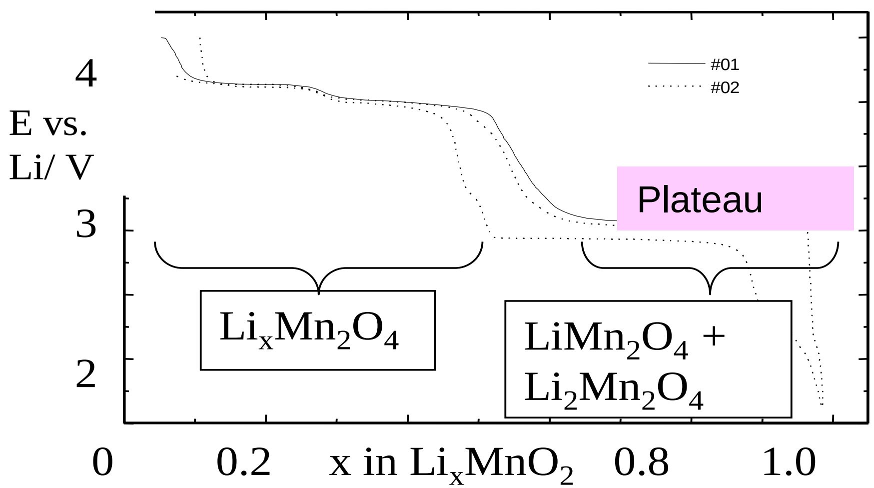
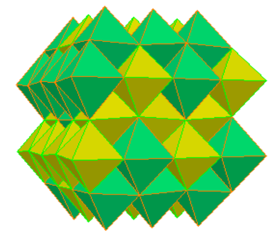


Spinel-type $Li_xMn_2O_4$





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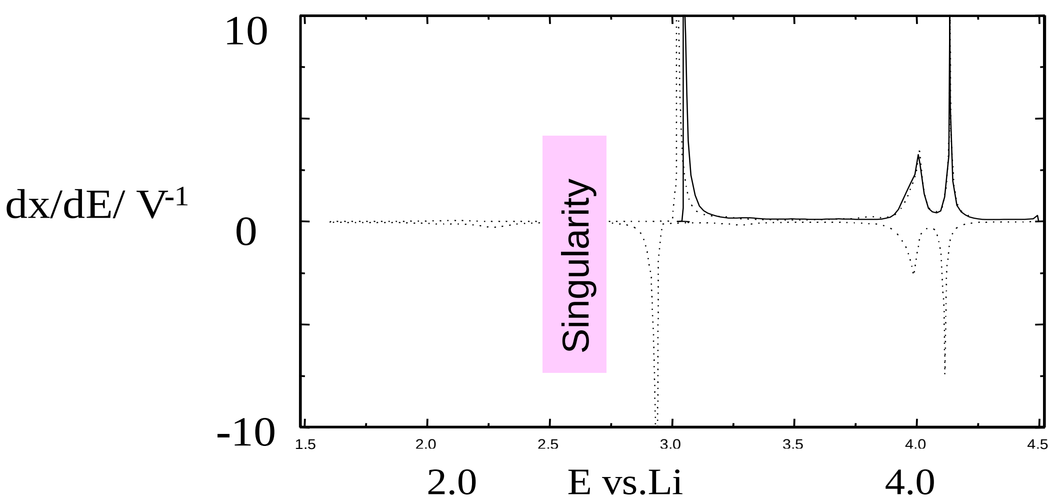

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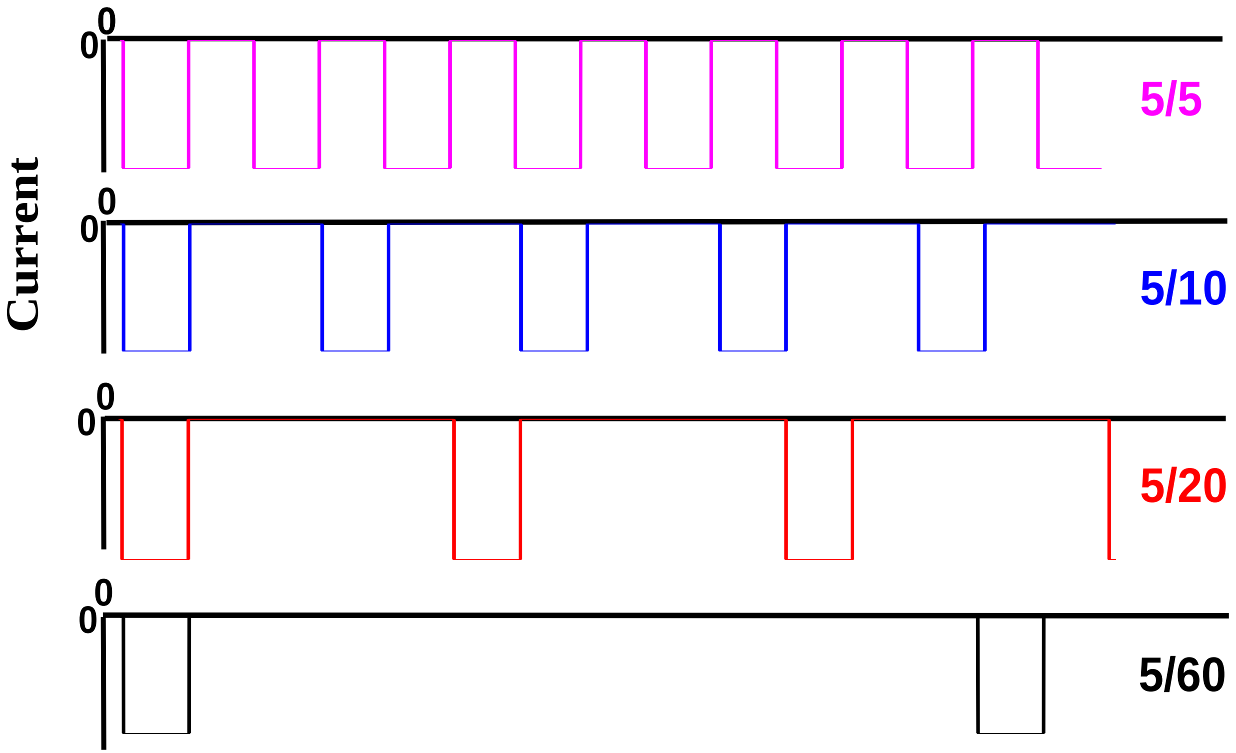
The Galvanostatic Intermittent Titration Technique (GITT)



Fick's laws of Diffusion and the Sand Equation for constant current

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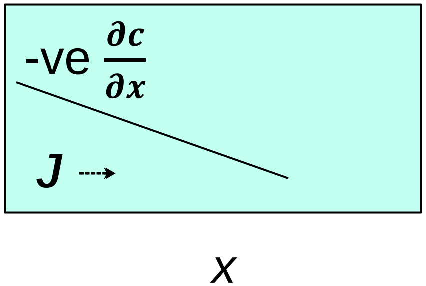
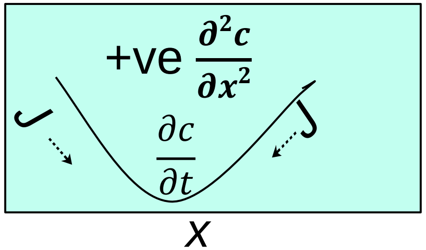


- 2nd law: $\dfrac{\partial c}{\partial t} = -\dfrac{\partial J}{\partial x} = \mathrm{D}\dfrac{\partial^2 c}{\partial x^2}$



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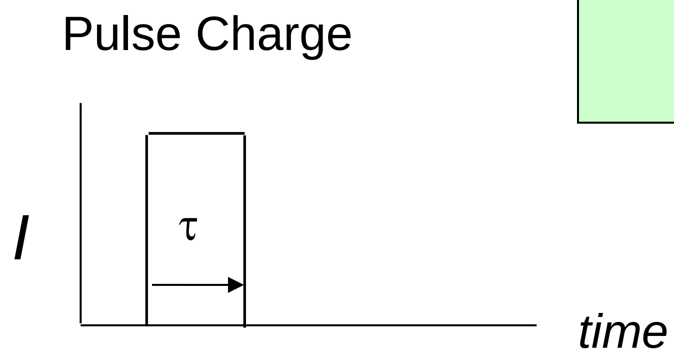
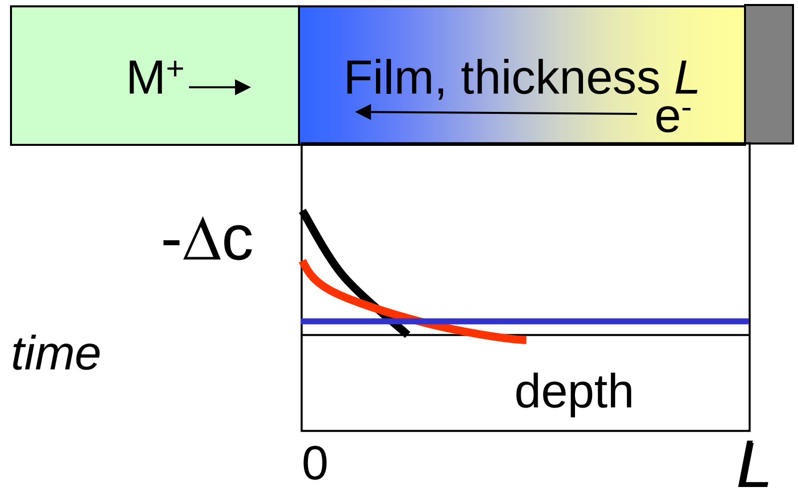
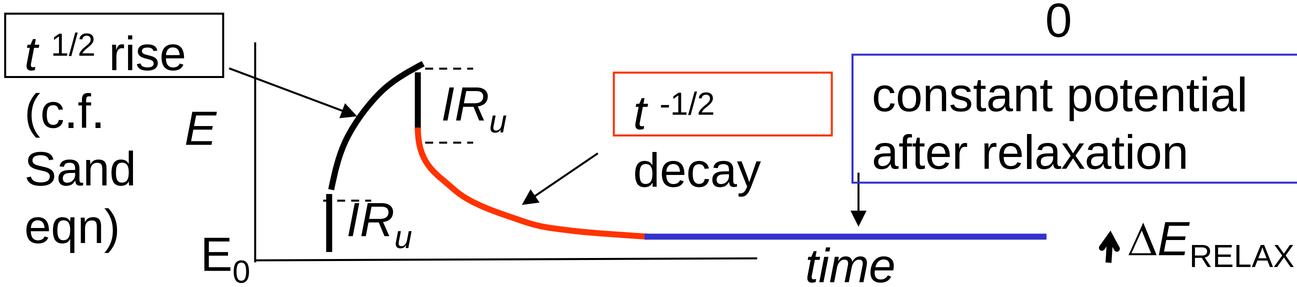
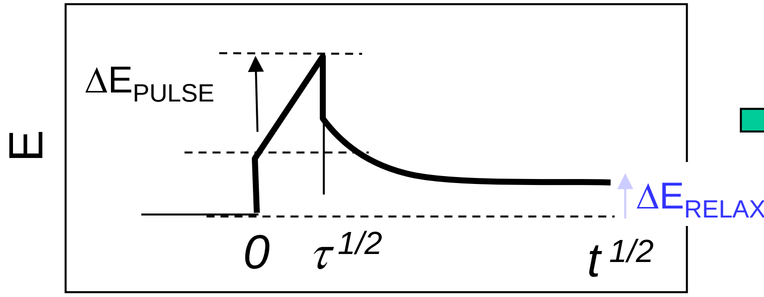
Current pulse analysis (GITT) to measure diffusion in single phase materials



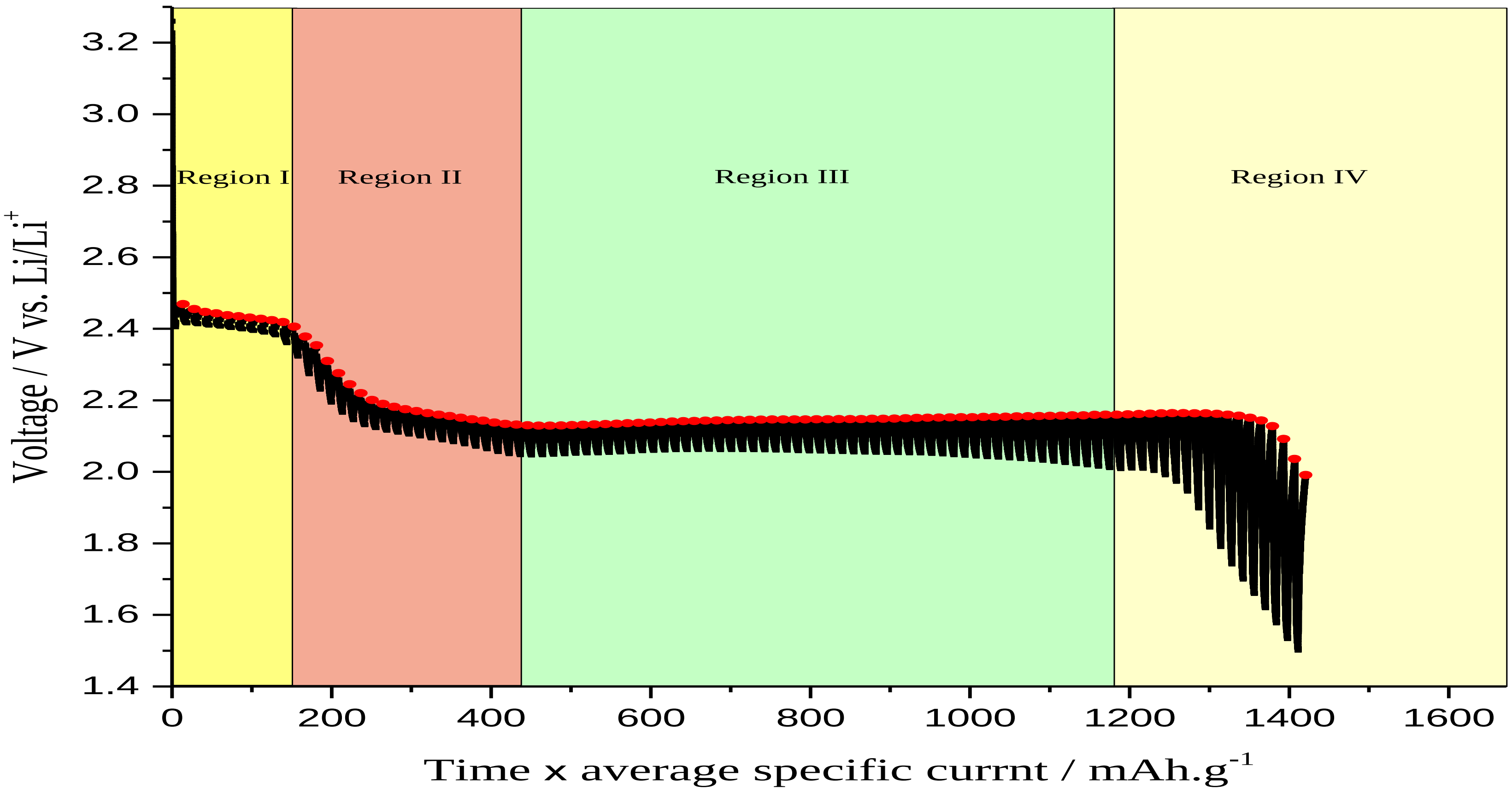






$$D = \left(\frac{4}{\pi}\right)\left(\frac{L^2}{\tau}\right)\left(\frac{\Delta E_{RELAX}}{\Delta E_{PULSE}}\right)^2$$

A complete titration



GITT profile for first discharge of Li/S cell using 5 min pulse and 10 min relaxation (5/10), with 1M LiTFSI in TEGDME/DOL. The red circles represent the last data point at the end of each relaxation period at discharge state of Li−S cell.

GITT also shows the thermodynamic discharge curve

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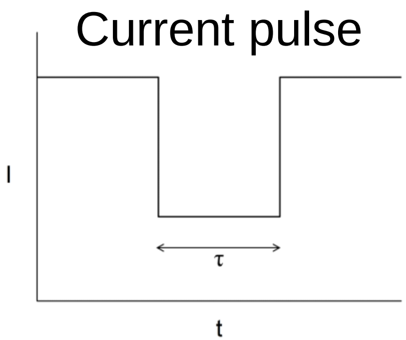
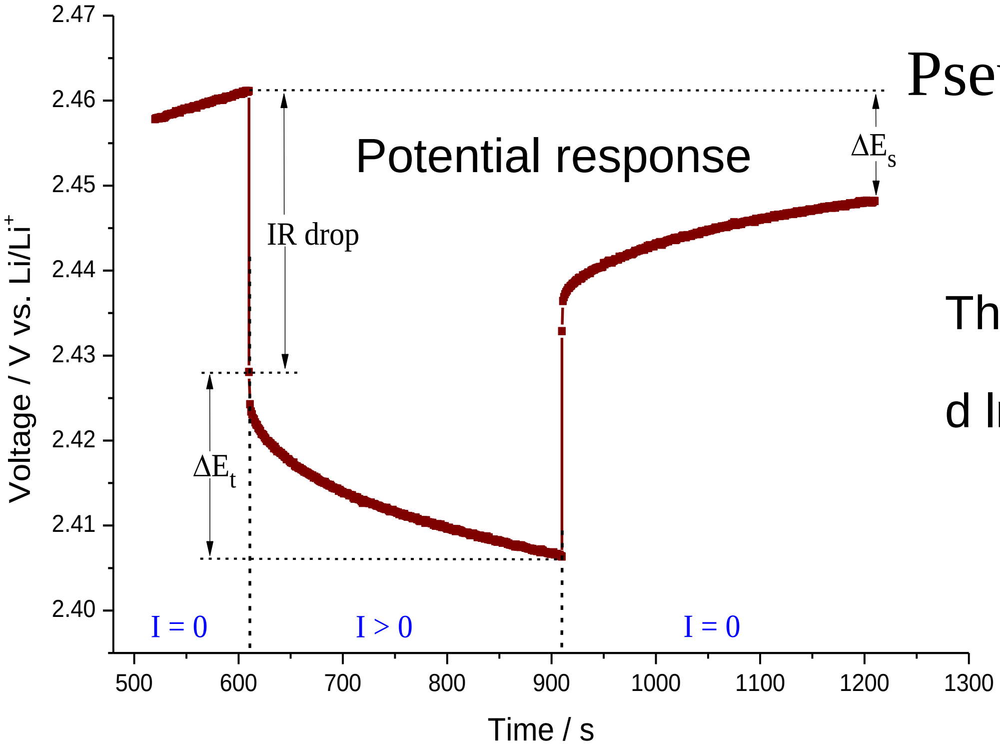
Further GITT analysis





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$$\text{Pseudocapacitance, } C_v = \frac{dq_v}{dEs}$$

Thermodynamic Factor

d ln a /d ln c $=\left(\frac{F^2 c}{RT}\right)\left(\frac{dE_S}{dq}\right)$

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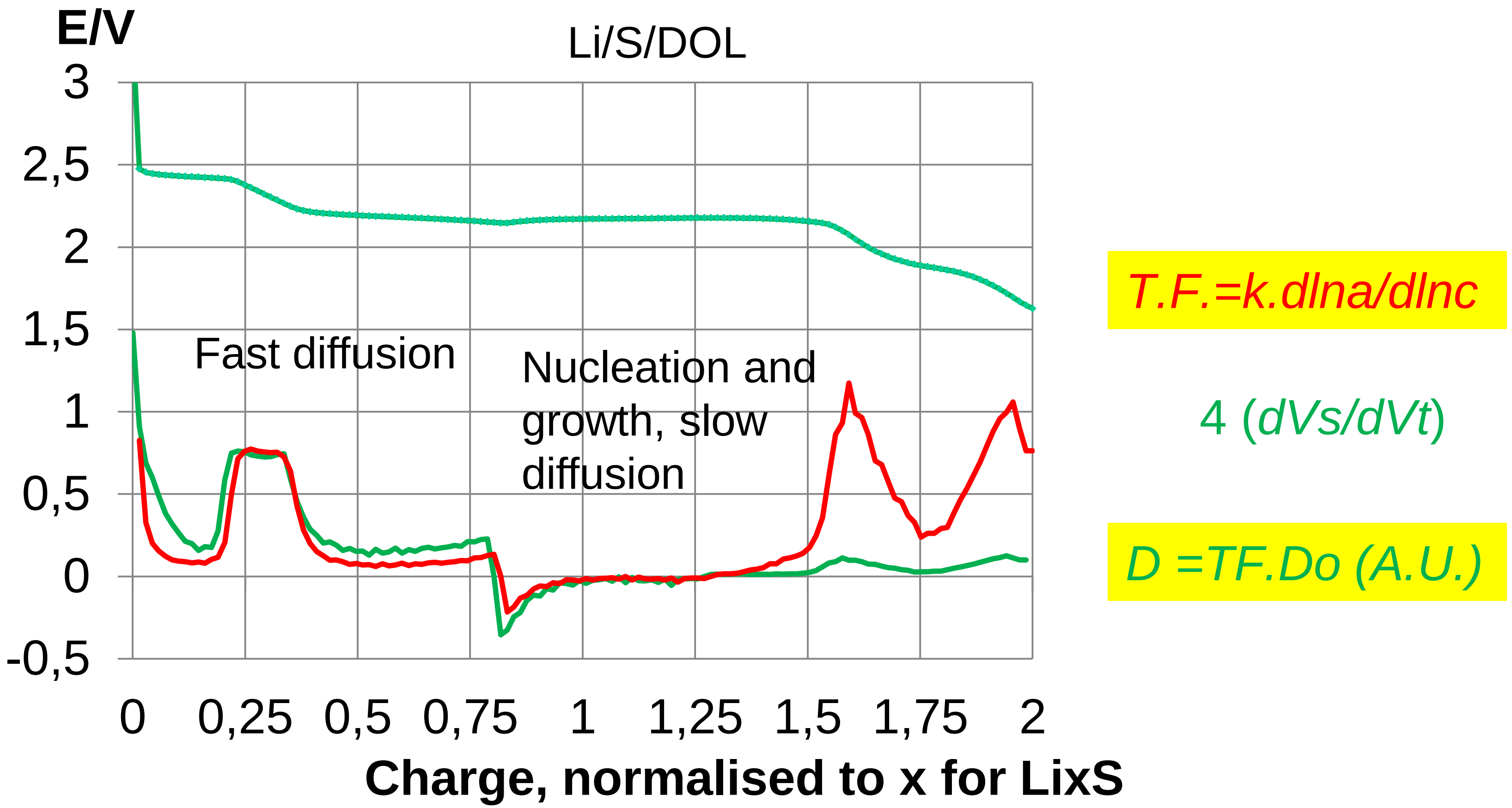
Relaxed Potential, Diffusion Coefficient, Pseudo-capacitance and Thermodynamic Factors from GITT



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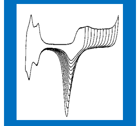
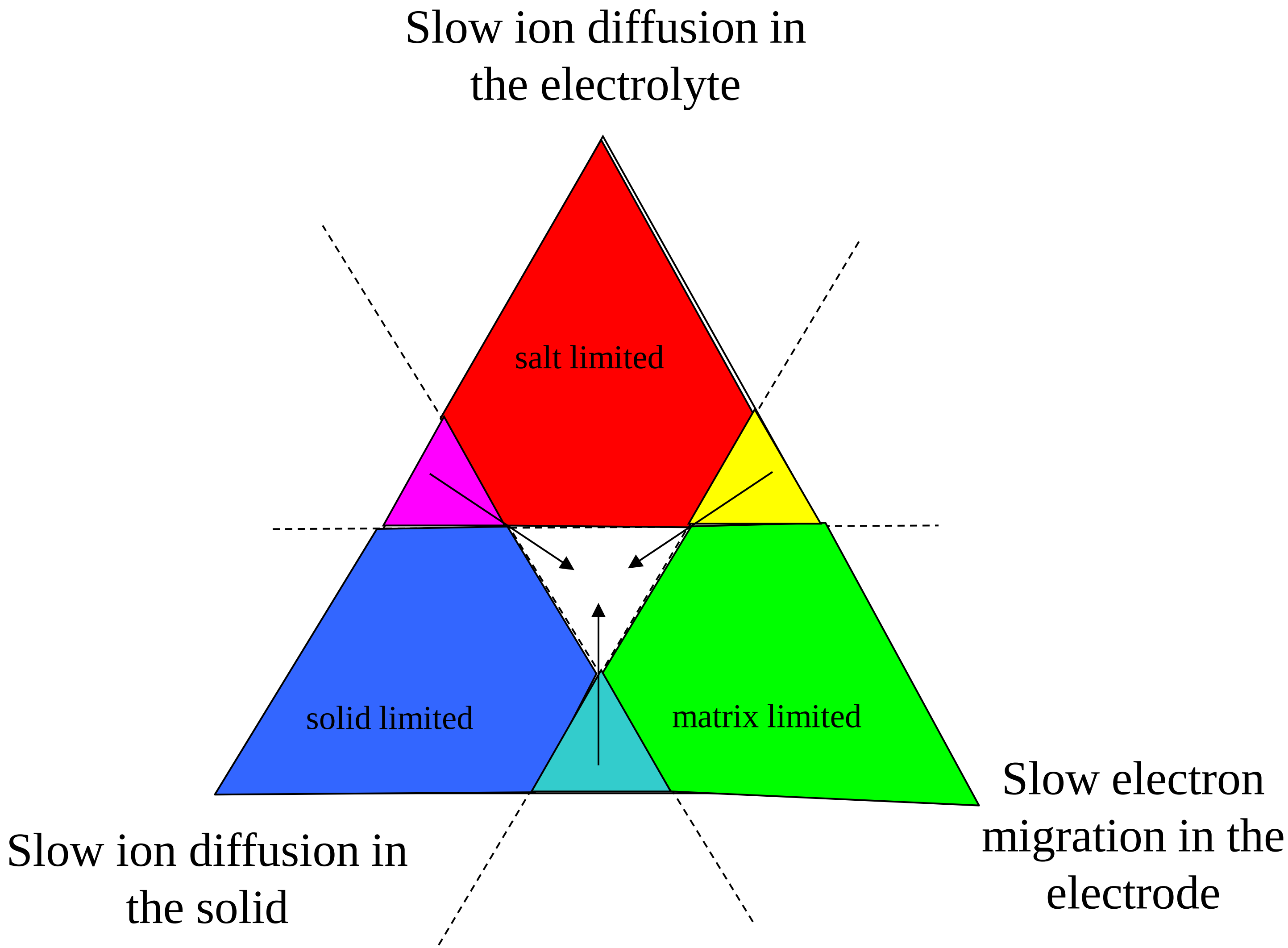


Conclusion – the rate limiting step rules !



Summary

- Normal cyclic voltammetry does not work well with battery cells
- Slow scan voltammetry gives a good overall picture of redox reactions and the useable potential range
- Derivative Coulometric Titration gives superior results
- GITT gives both Thermodynamic and Diffusion data

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