

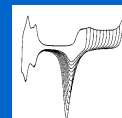
Basic Electrochemistry

with a focus on lithium ion
batteries

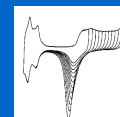
John R Owen at



SEPTEMBER 17-20, 2018
SALA D'ACTES CARLES MIRAVITLLES
ICMAB-CSIC, Bellaterra, Spain



Term	Description	Unit
v	Voltage or potential	V
E_e^0 or E^0	Standard potential	V
$E^0(\text{Ox/R})$	Standard potential of the Ox/R redox couple	V
F	Faraday's constant	C mol ⁻¹
n	number of electrons involved in an electrochemical reaction	/
ΔG	free energy change	J mol ⁻¹
C	number of moles involved in an electrochemical reaction	mol
t	time	s
Q	charge	C
I	current = dQ/dt	A
c_i	concentration of species 'i'	mol cm ⁻³
V	volume	cm ³



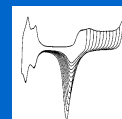
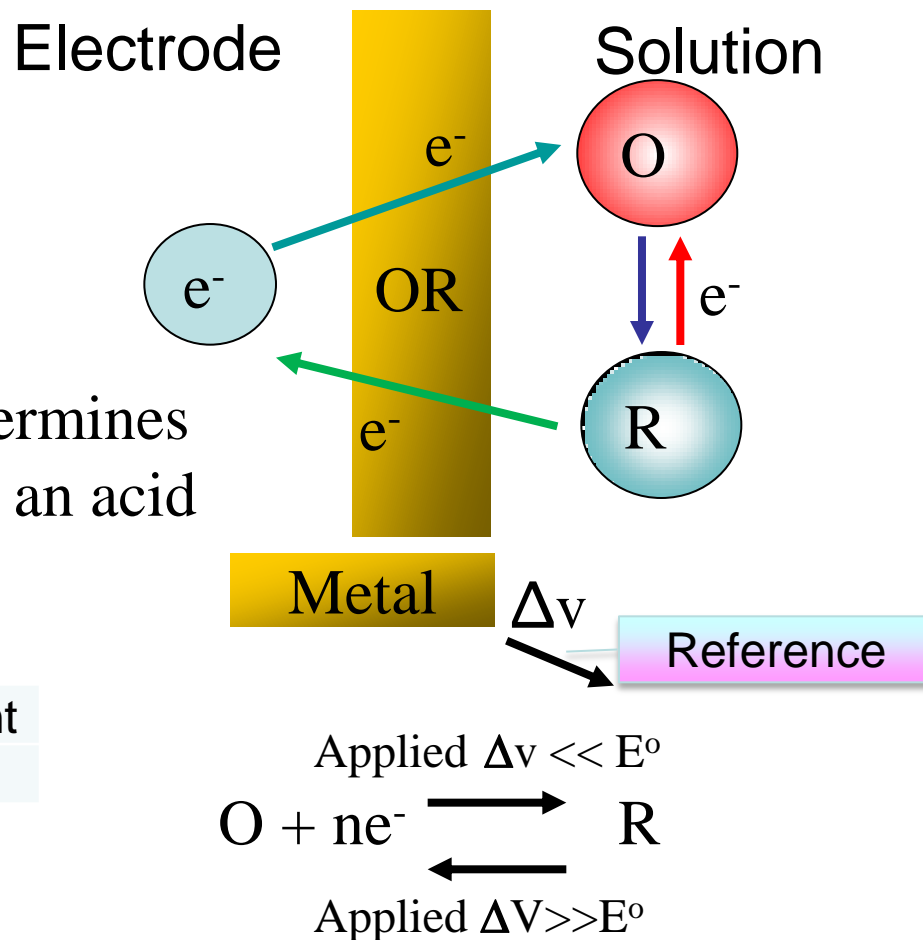
Redox Reactions

OR

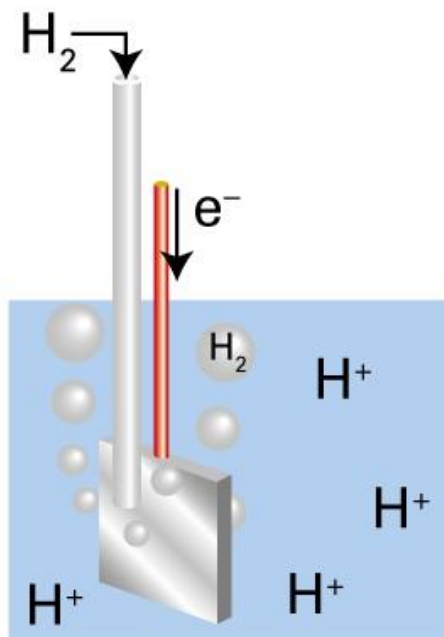
Applied potential, v vs.
Electrode Potential, E determines
reaction direction, e.g. for an acid
at pH0, $E = E^0$

Oxidant	E^0	Reductant
$H^+ + e^-$	0.00	$\frac{1}{2} H_2$

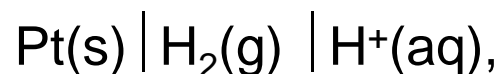
Therefore at negative potentials
Hydrogen is evolved.



Reference electrodes

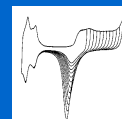


- Only the potential difference across a cell can be measured
- Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode



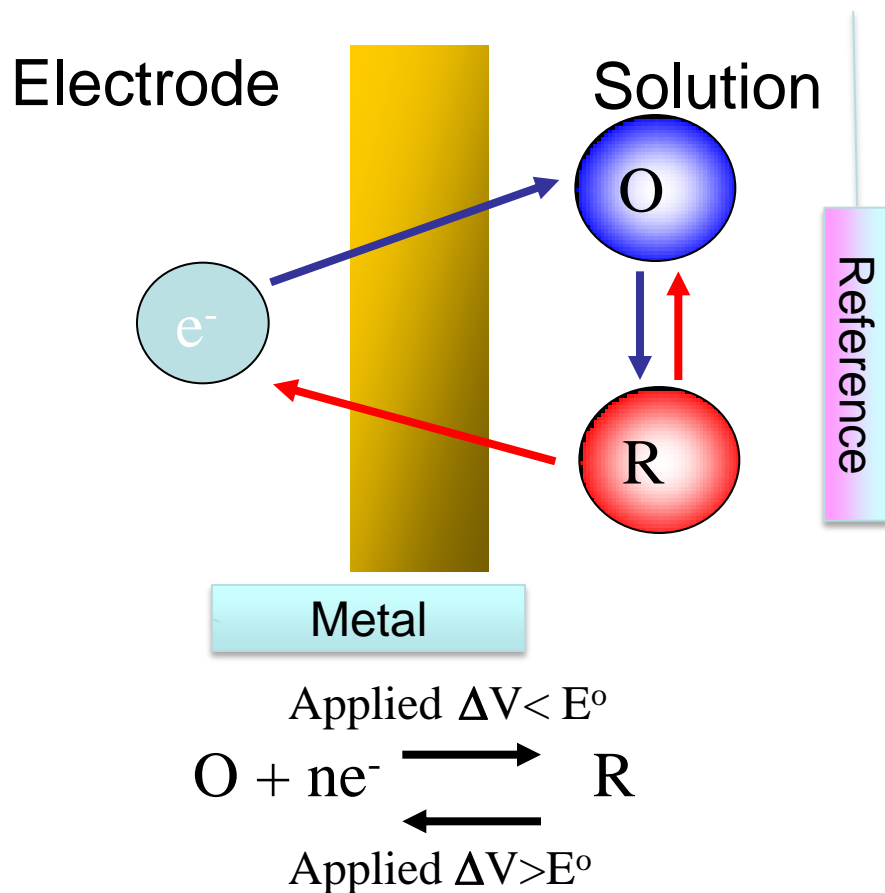
$$E_{\text{cell}}^0 = 0 \text{ V} \quad a_{\text{H}^+} = 1$$

$$a_{\text{H}_2} = 1$$



The Electrochemical Series

Oxidant	E°	Reductant
$F_2 + 2e^-$	3.05	$2F^-$
$Cl_2 + 2e^-$	1.72	$2Cl^-$
$Co^{3+} + e^-$	1.92	Co^{2+}
$O_2 + 4H^+ + 4e^-$	1.23	$4OH^-$
$Ag^+ + e^-$	0.80	Ag
$Fe^{3+} + e^-$	0.77	Fe^{2+}
$Cu^{2+} + 2e^-$	0.34	Cu
$H^+ + e^-$	0.00	$\frac{1}{2} H_2$
$Ti^{3+} + e^-$	-0.44	Ti^{2+}
$Zn^{2+} + 2e^-$	-0.44	Zn
$Al^{3+} + 3e^-$	-1.68	Al
$Mg^{2+} + 2e^-$	-2.36	Mg
Na^+	-2.71	Na
Li^+	-3.04	Li

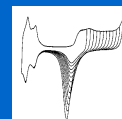


Reduction Potentials vs. Standard Hydrogen Reference Electrode SHE at pH0, 1atm H_2 , 0°C

The more positive E° the more oxidising the oxidised form

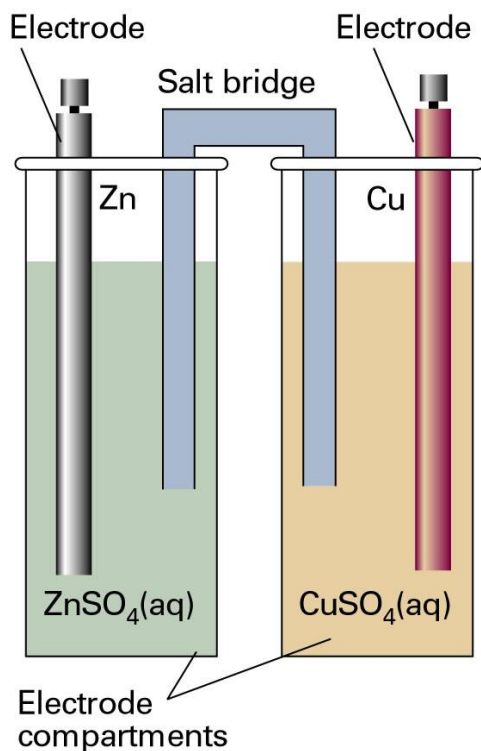
The more positive E° the more reducing the reduced form

E° values are measured or compared in electrochemical cells with **reference electrodes**.



Electrochemical cells asleep

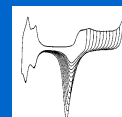
(Daniel cell)



- Open circuit cell is in equilibrium
- Anode reaction (corresponding to oxidation)
 - $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-}$
- Cathode reaction (reduction)
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Cu(s)}$
- $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu(s)}$
- $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}} = 1.10 \text{ V}$

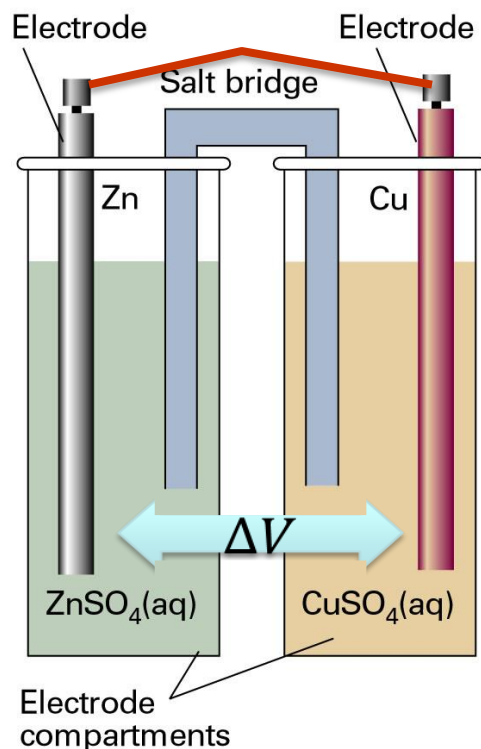
Equilibrium sign

- $\Delta_r G = -nFE^0_{\text{cell}}$ where
- $F = 96485 \text{ C mol}^{-1}$
- n : number of electrons



Electrochemical cells working

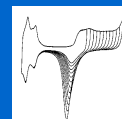
(Daniel cell)



$$E^0 (\text{Cu}^{2+}/\text{Cu}) = +0.340 \text{ V},$$

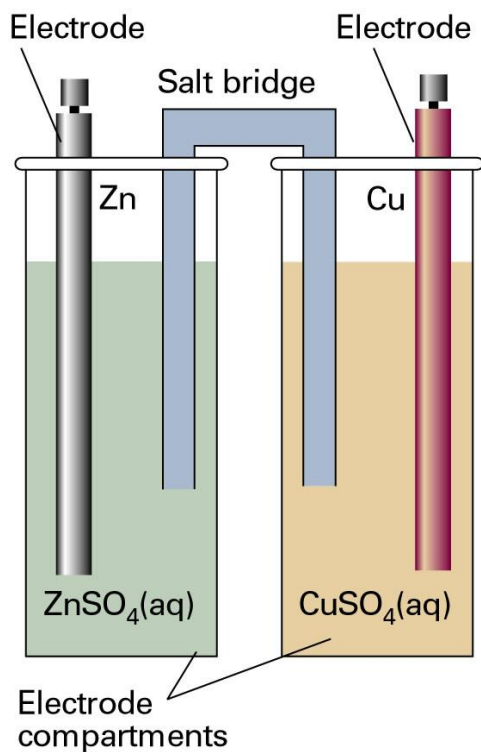
$$E^0 (\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ V}.$$

- What happens once the cell is connected (for instance, connect the two electrodes with a cable)?
- Potential difference ΔE appears across the electrolyte
 - $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
 - $\text{Zn}(\text{s}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
 - Cations will go from the Zn compartment (anode) to the Cu compartment (cathode)
 - Anions will go in the opposite direction
 - current $I = \Delta V / R$ where
 - $R = \text{total resistance}, \Delta V \approx \Delta E$

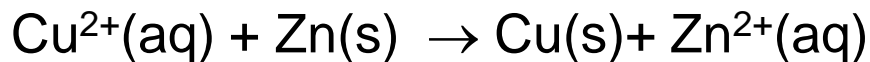


Electrochemical cells

PROBLEM



Question: calculate the standard Gibbs energy of the reaction:



taking into account that, for **each** electrochemical reaction:

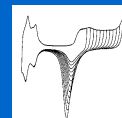
$$\Delta_r G(\text{reduction}) = -nFE^0$$

where F is Faraday's constant, n is the number of electrons and E^0 is the standard potential.

Answer: -212.8kJ/mol

$$E^0 (\text{Cu}^{2+}/\text{Cu}) = +0.340 \text{ V},$$

$$E^0 (\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ V}.$$

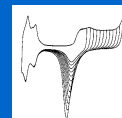


Chemical Redox reactions

PROBLEM

What would happen if I immerse a Zn metal bar into a solution containing Cu^{2+} ?

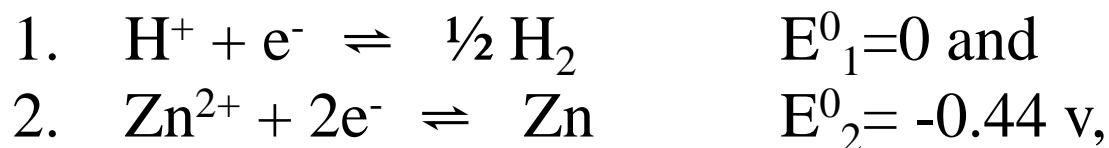
Answer: $\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$
because $E^0 (\text{Cu}^{2+}/\text{Cu}) > E^0 (\text{Zn}^{2+}/\text{Zn})$



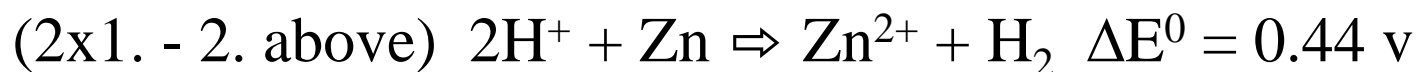
Chemical Redox Reactions

PROBLEM

- Consider the mixing of two redox reagents O1 and R2 where

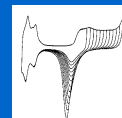


- If $E^0_1 > E^0_2$ they should react:



because

- Zn is a more powerful reductant than H_2
- $\Delta G = -nFE = -0.88 \times 96485 \approx -85 \text{ kJ mol}^{-1}$



Chemical Redox reactions

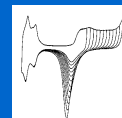
What reaction will happen if I mix $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Ru}(\text{CN})_6^{3-}$?

Note that $E^0 = 0.36 \text{ V}$ for $\text{Fe}(\text{CN})_6^{4-} / \text{Fe}(\text{CN})_6^{3-}$ system and $E^0 = 0.52 \text{ V}$ for $\text{Ru}(\text{CN})_6^{4-} / \text{Ru}(\text{CN})_6^{3-}$ system.

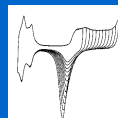
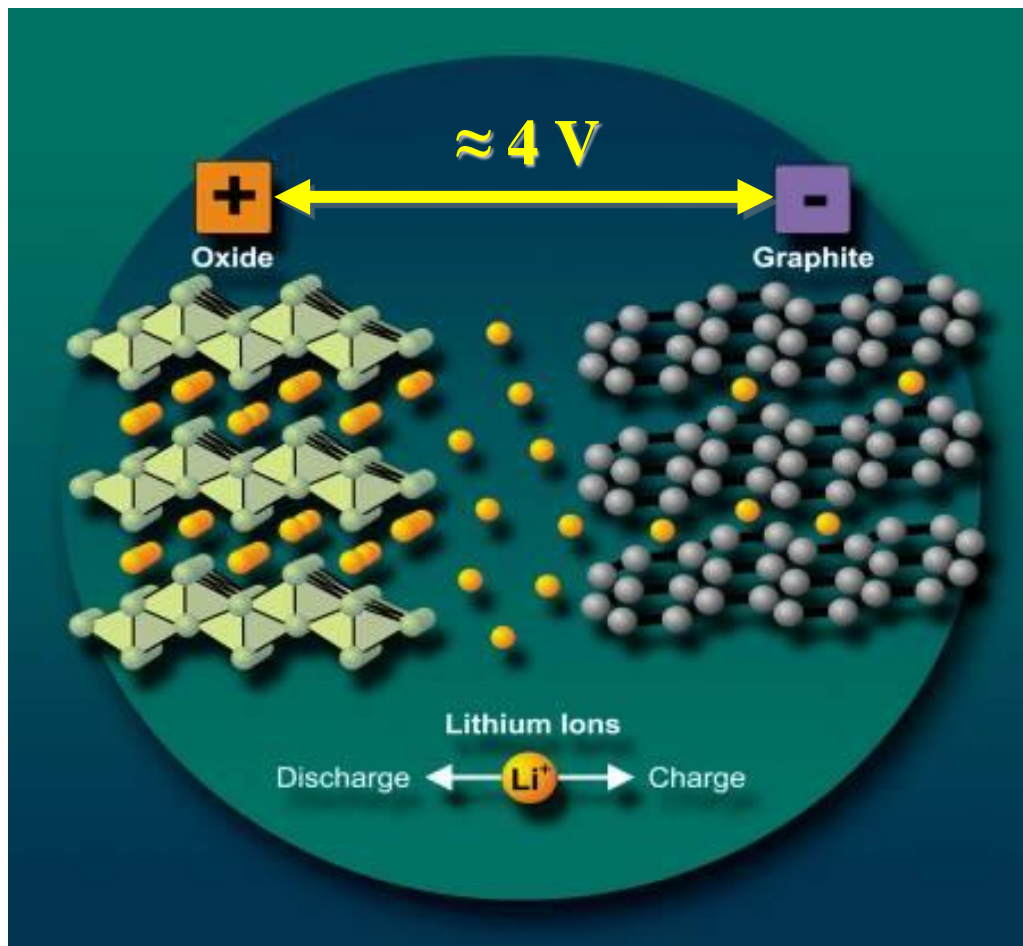
Identify O and R in each case

Determine which are the most powerful O and R

Answer: $\text{Ru}(\text{CN})_6^{3-} + \text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Ru}(\text{CN})_6^{4-} + \text{Fe}(\text{CN})_6^{3-}$



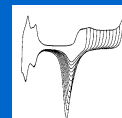
Rocking chair battery



Anode and Cathode

	Anode	Cathode
General Definition	oxidation	reduction
Galvanic cell, Fuel cell, primary battery	negative electrode	positive electrode
Electrolyser	Positive electrode	negative electrode
Secondary (rechargeable) battery	Negative on discharge positive on charge ¹	Positive on discharge negative on charge
Secondary battery industrial jargon	Always negative during normal operation	Always positive during normal operation

¹ Because the direction of the reaction changes from discharge to charge



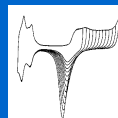
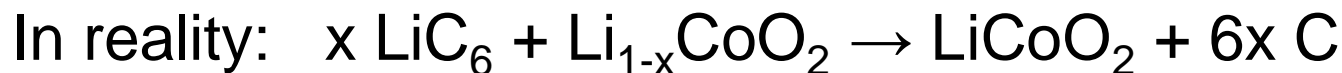
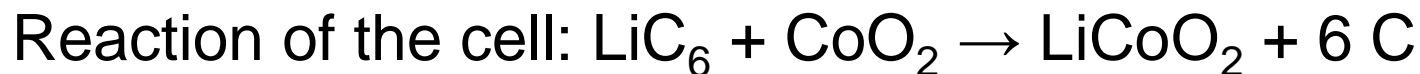
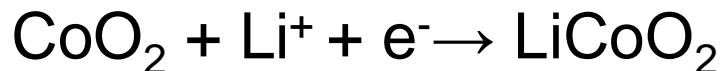
Lithium Ion Battery

PROBLEM

Write down the spontaneous (discharge) reaction of a battery made of a LiCoO_2 positive electrode and a graphite negative electrode

Note that $E^0 \approx 4\text{V}$ vs. Li^+/Li for $\text{LiCoO}_2/\text{CoO}_2$ and $E^0 \approx 0\text{V}$ vs. Li^+/Li for LiC_6/C

Answer:



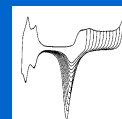
Lithium Ion Battery

Write down the reaction to **recharge** a battery made of a LiCoO_2 positive electrode and a graphite negative electrode

Answer:



This is achieved by applying a potential higher than ca. 4 V to the whole battery to “force” the electrons to go from the LiCoO_2 electrode to the graphite electrode.



Faraday's law

charge \swarrow $Q = n F m$ \searrow Number of moles

Note that F has units of coulombs per mole of electrons

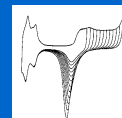
Example:

Calculate the number of Ah of charge available from a lithium metal negative electrode weighing 1 g, assuming an atomic mass [Li] = 7g

Answer:

Number of moles Li, $m = 1/7$. Li to Li⁺ $n=1$

$Q = 96485/7 \text{ C} = 96485/(7*3600) \text{ Ah} \sim 3.8 \text{ Ah}$



Faraday's law

PROBLEM

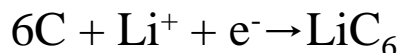
1. Calculate the mass of LiFePO_4 required to act as the positive electrode of a 4 Ah lithium ion cell, assuming the charge reaction is



Use atomic masses/g Li = 7, Fe= 56, P= 31, O = 16

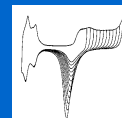
Hint - Convert 4Ah into Coulombs,
then moles, then grams

2. Calculate the mass of graphite required to act as the negative electrode of a 4 Ah lithium ion cell, assuming the charge reaction is



Use atomic masses/g C= 12, Li= 7

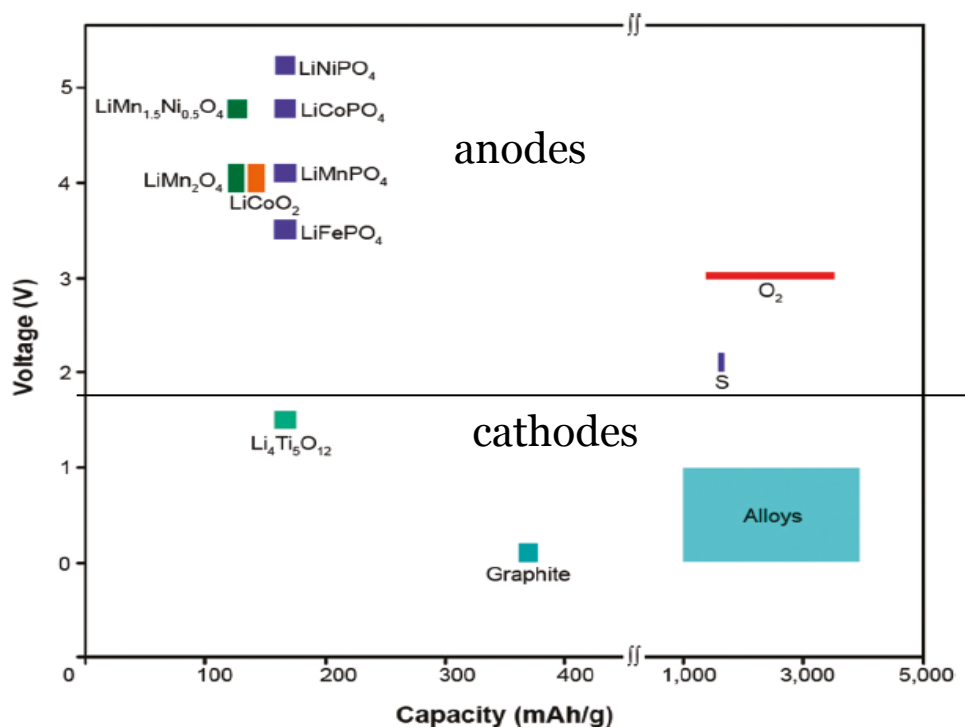
3. Calculate the specific capacity (Ah/g) for each electrode.



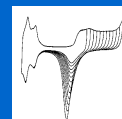
A choice of cathodes and anodes

High Voltage Li-ion batteries have a high energy density

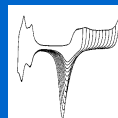
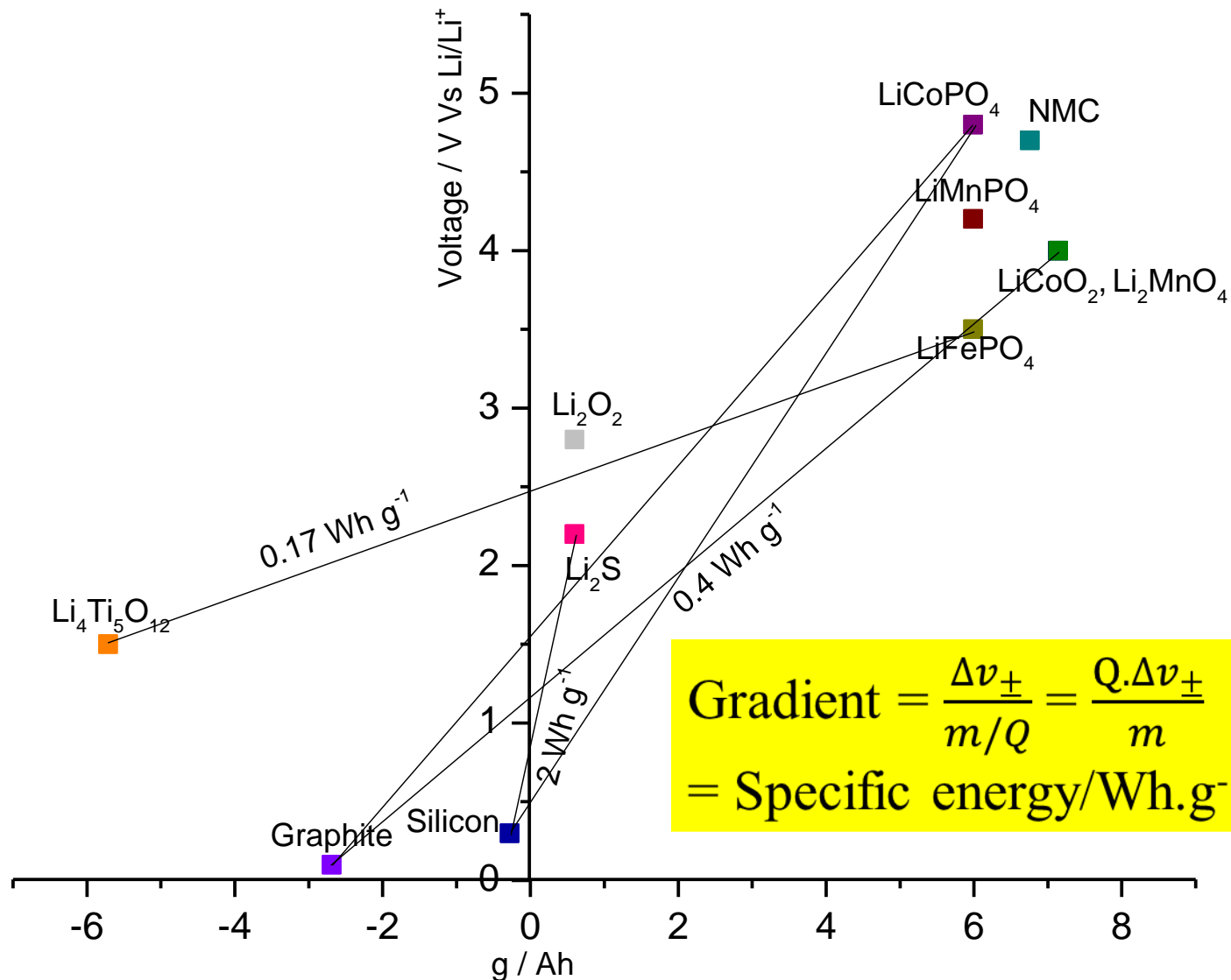
Specific Energy = Potential difference x (charge per mass)



A. Manthiram, *The Journal of Physical Chemistry Letters*, 2011, **2**, 176–184.



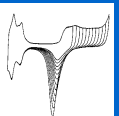
Specific Energy, Owen Plot



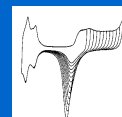
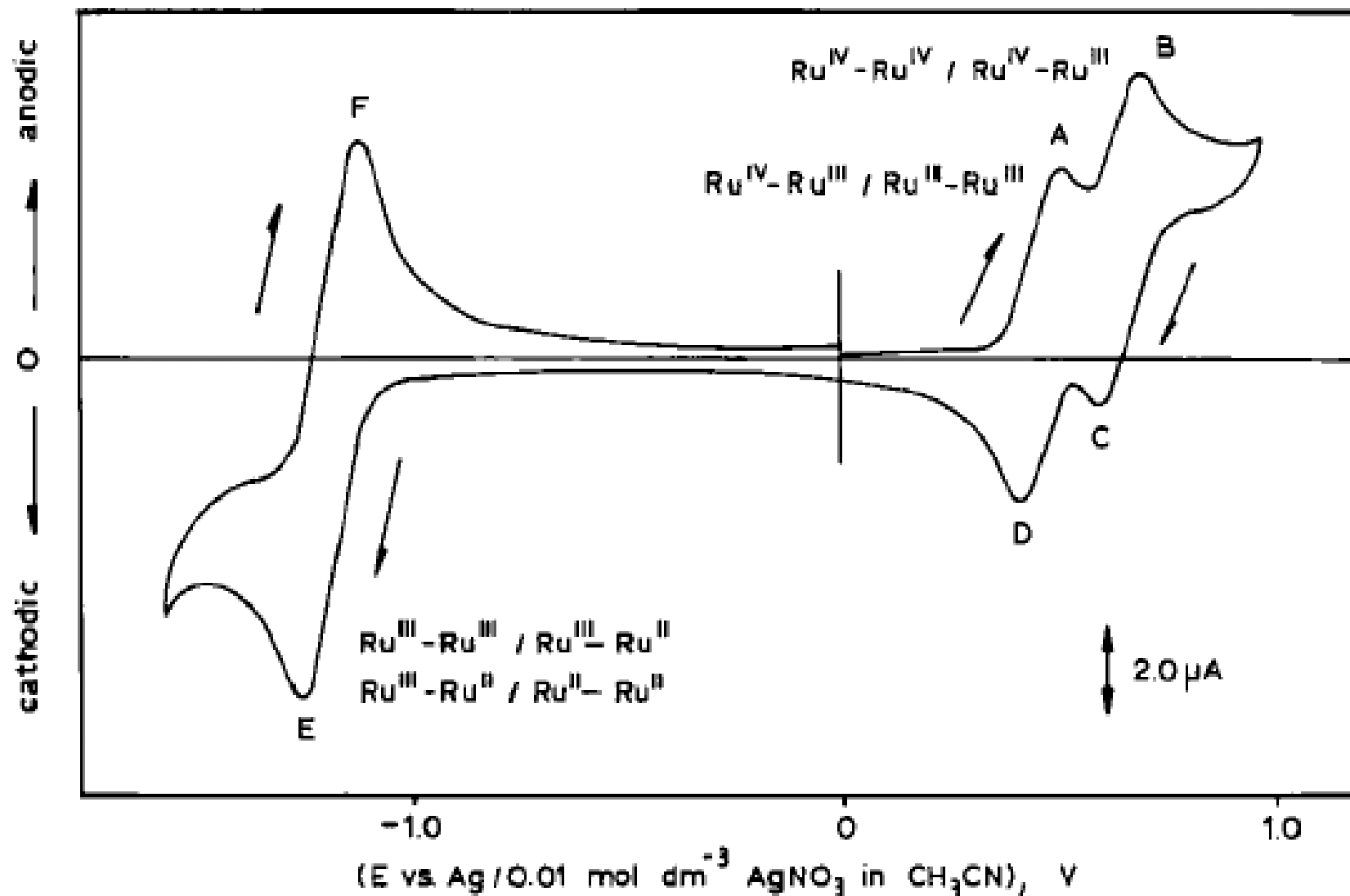
Cyclic Voltammetry (CV)

- This technique applies a scanning voltage to a cell while measuring the current. When the top of the chosen voltage range is reached, the scan is reversed.
- Current peaks identify the potentials at which anodic and cathodic reactions occur according to

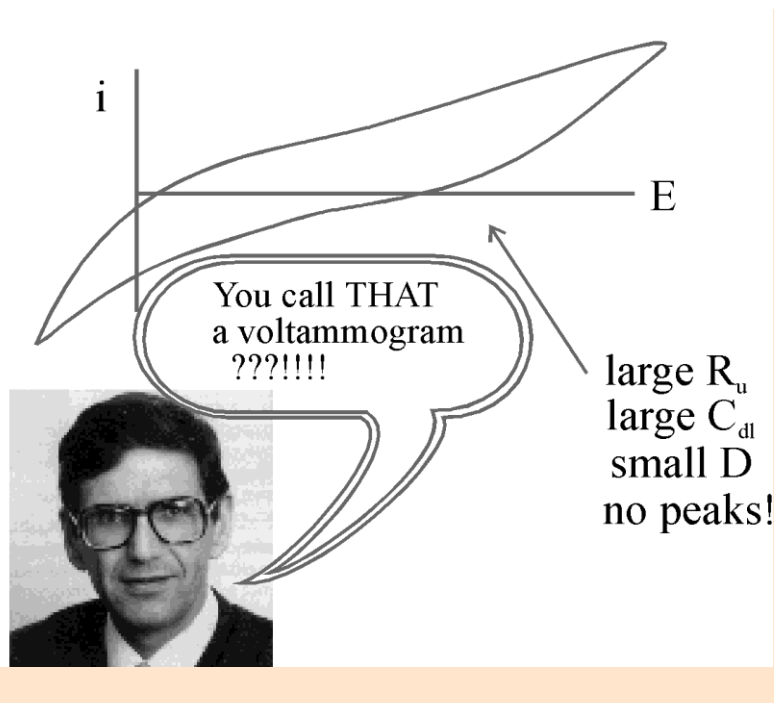
current \swarrow $I = n F \frac{dm}{dt}$ \searrow Reaction rate



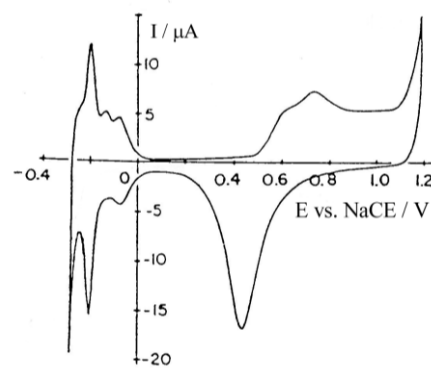
A Cyclic Voltammogram



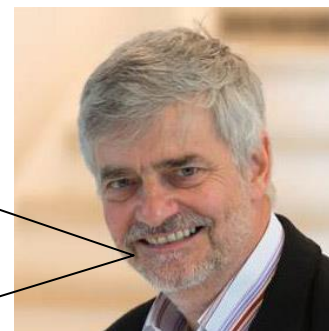
Electrochemical Techniques for the Characterisation of Solids, c. 1991



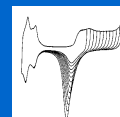
Prof D Pletcher
c. 1991



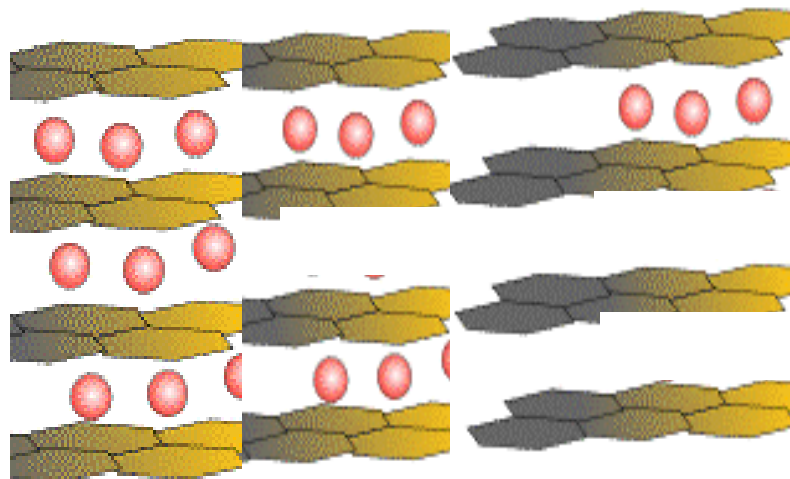
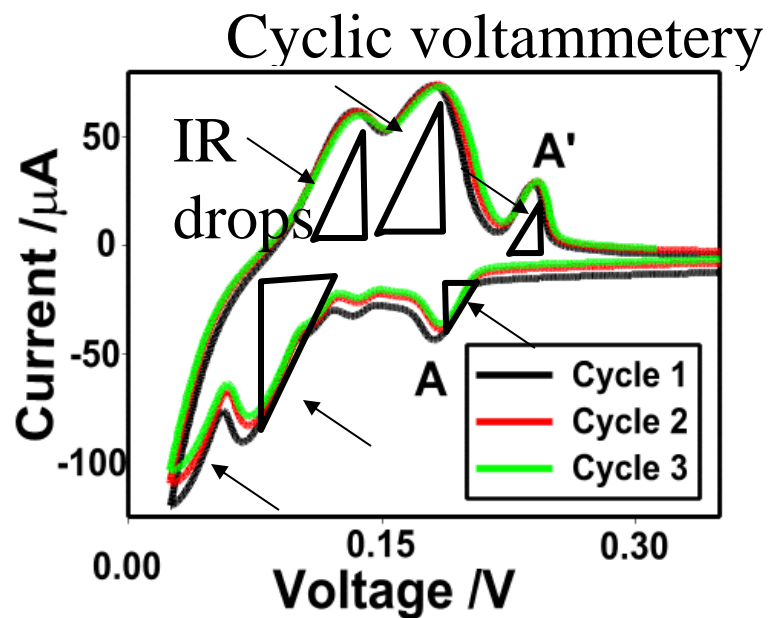
Here's one
I did in
junior
school
Ha!Ha!



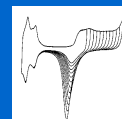
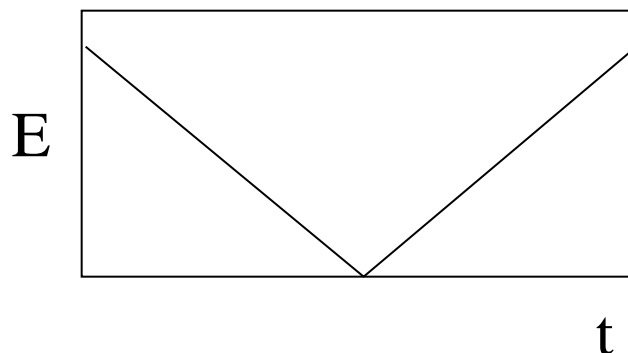
Prof P N Bartlett
c. 2010



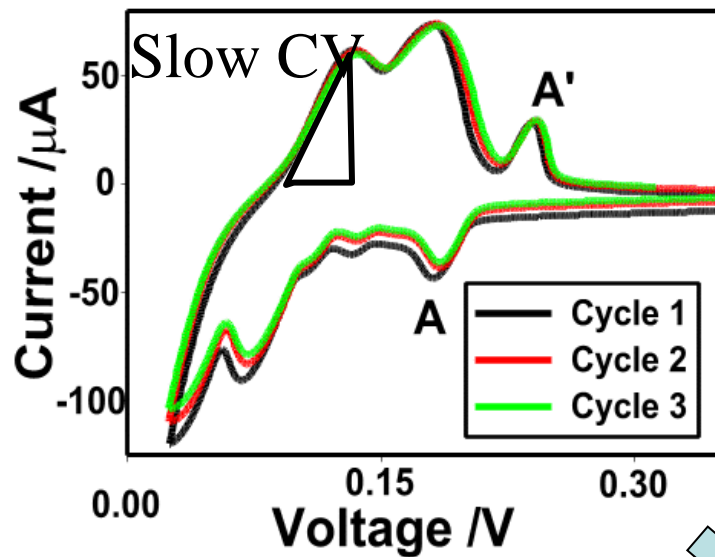
Phase changes in graphite



Problem : In CV the IR Drop increases with I



What went wrong?



Capacitance per volume

$$C_v \sim F \times 15M$$

Resistance

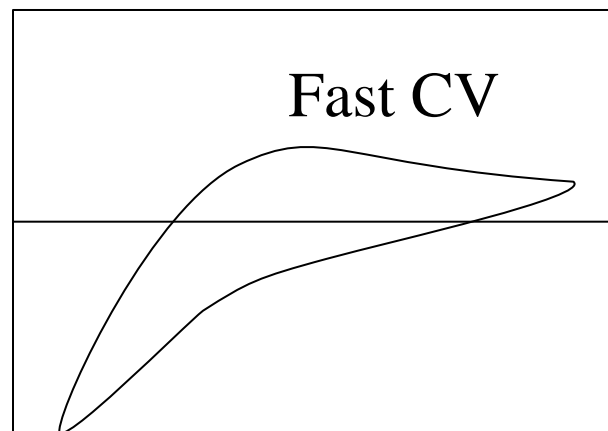
(nonaqueous electrolyte)

$$R \sim 10 \text{ k}\Omega$$

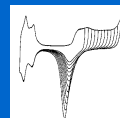
Minimum feature resolution

$$\Delta V > \text{scan rate} \times RC$$

$$\text{or } \Delta V > \text{scan rate} \times \frac{L^2}{D}$$

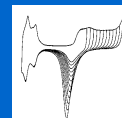


Voltage / V

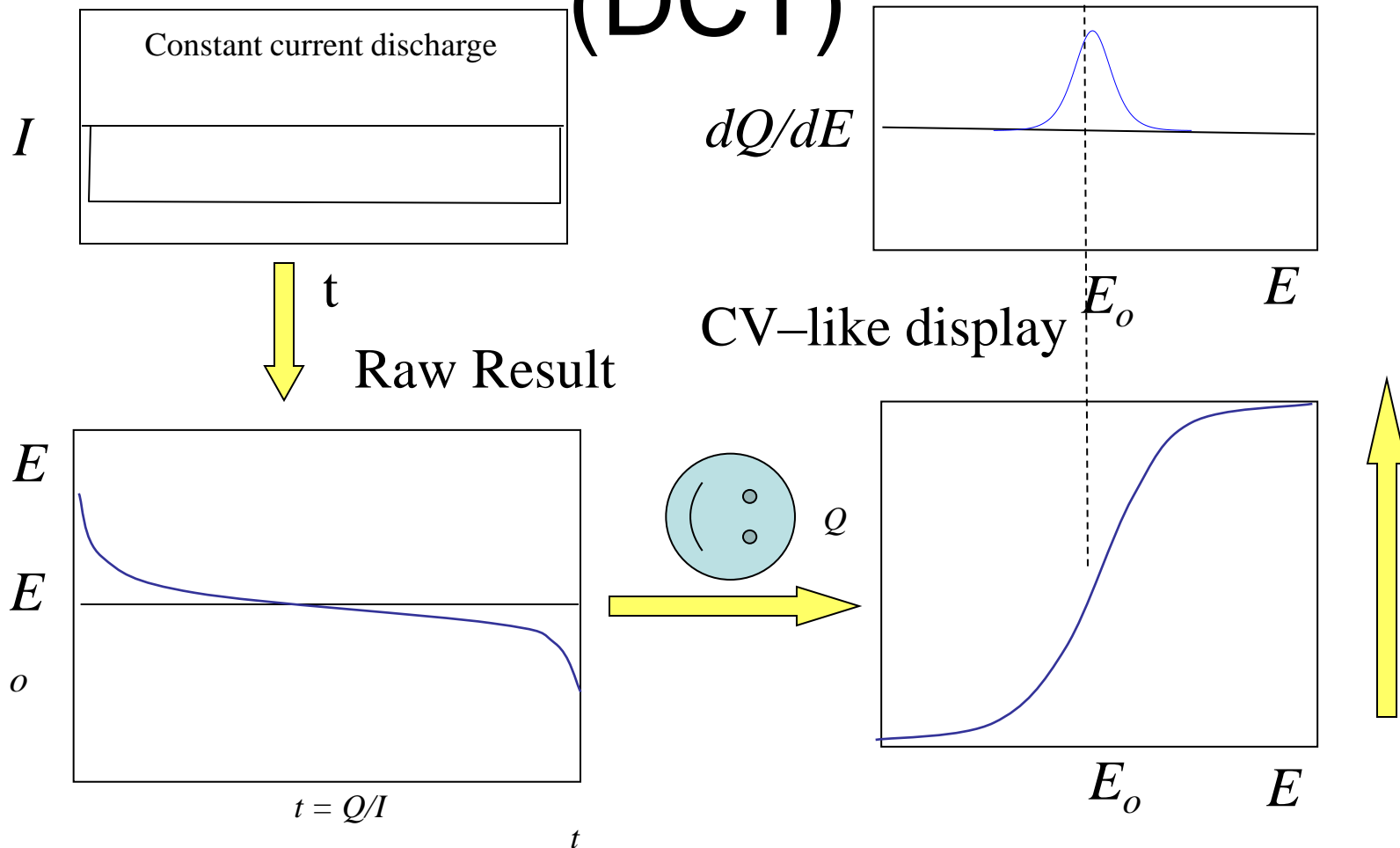


Let's Try Another Way!

*Derivative (differential)
Coulometric
Titration*



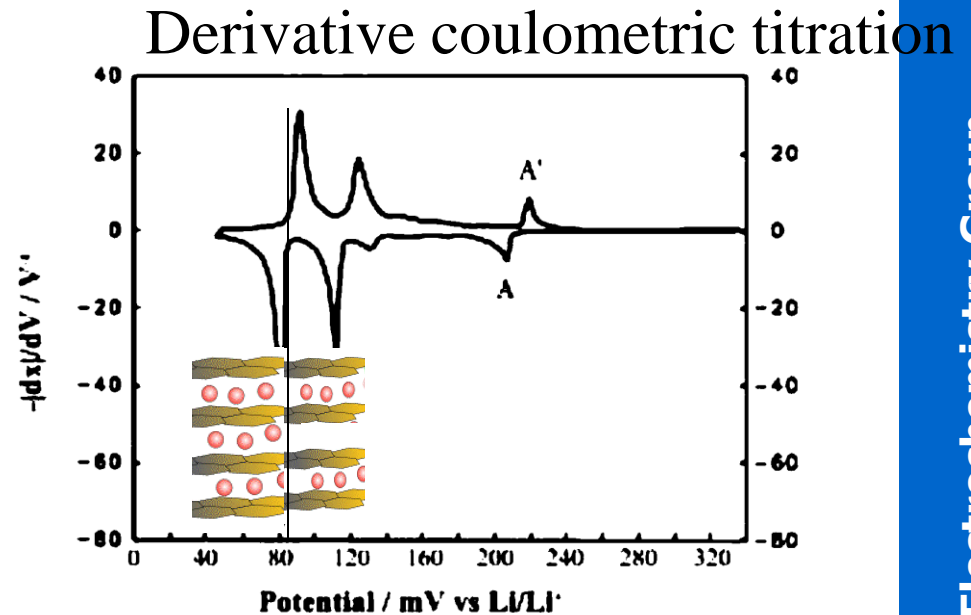
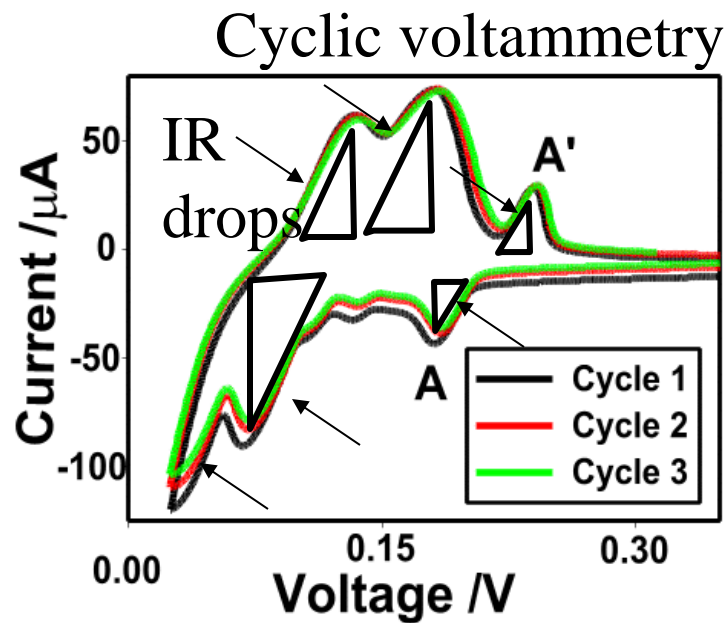
Derivative Coulometric Titration (DCT)



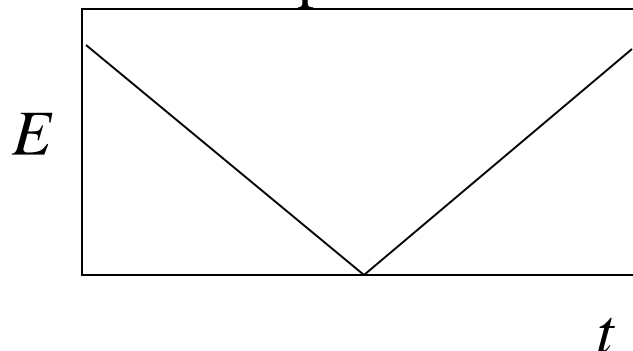
IR drop is constant - does not increase toward peak top



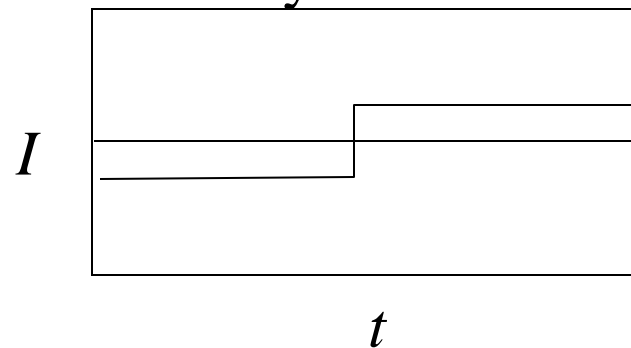
SSSCV vs DCT for Graphite



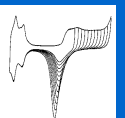
IR Drop increases with I



Always small IR Drop \checkmark



Derivative coulometric titration is better than CV for thermodynamic data



Summary

- Electrochemical and Chemical redox reactions explained
- Electrode potential measured *vs* a Reference Electrode
- Faraday's law shows the Theoretical Specific Energy
- Cyclic voltammetry identifies potentials roughly.
- Differential Coulometric Titration gives better resolution of voltage peaks.

