

2. Principles determining the voltages and capacities of electrochemical cells (Huggins, ch. 2)

1. Thermodynamic properties of individual species
2. A simple example: lithium/iodide cell
3. The shape of discharge curves and Gibbs phase rule
4. The coulometric titration technique

1. Thermodynamic Properties of Individual Species

-If there is no current flowing, this chemical driving force is balanced by an electrical driving force in the opposite direction

-Chemical potential of species i in a phase j

$$\mu_i = \partial G_j / \partial n_i$$

G_j : the molar Gibbs free energy of phase j,
 n_i : mole fraction of the i species in phase j

-Integral form, $\Delta\mu_i = \Delta G_i$

$$\Delta\mu_i = -z_i F E$$

z_i : the number of elementary charges carried by particles

-Chemical potential of a given species is related to another thermodynamic quantity, its *activity*, a_i

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

where μ_i° : a constant, in its standard state

R : gas constant (8.315 J/mol K), T(K)

-Activity: effective concentration

→ $a_i = 1$ for pure i,

$a_i = 0.5$ for half species i (half chemically inert)

-Electrochemical cell

$a_i(-)$ in the negative electrode, $a_i(+)$ in the positive electrode

$$\mu_i(+) - \mu_i(-) = RT[\ln a_i(+) - \ln a_i(-)] = RT \ln[a_i(+) / a_i(-)]$$

$$E = -(RT/z_i F) \ln[a_i(+) / a_i(-)] \quad \text{Nernst equation}$$

2. A Simple Example: The Lithium/Iodine Cell

- A lithium/iodine (Li/I_2) cell
 - Currently widely used in cardiac pacemakers (primary battery)
 - Metallic lithium as the negative electrode
 - A composite of iodine with about 10 wt% of poly-2-vinylpyridine (P2VP) as positive → P2VP acting as an electron donor, and iodine as an acceptor
 - Solid LiI as a solid electrolyte
- (-) $\text{Li}/\text{electrolyte}/\text{I}_2(+)$

Virtual reaction (가상반응), $\text{Li} + \frac{1}{2}\text{I}_2 \rightarrow \text{LiI}$

$$E = -\Delta G_r/z_i F$$

where

$$\Delta G_r = \Delta G_f(\text{LiI}) \text{ and } z_i \text{ is } +1 \text{ for Li}^+$$

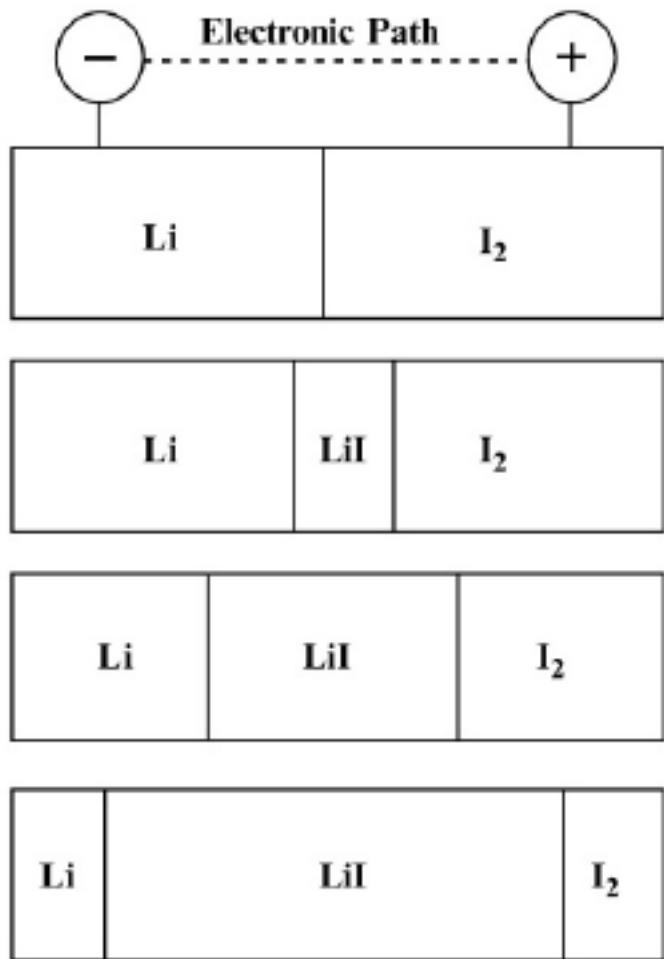


Fig. 2.1 Schematic representation of the microstructure of a Li/I_2 cell at several stages of discharge

$$\Delta G_f(Li) = -269.67 \text{ kJ/mol at } 25^\circ\text{C} \rightarrow 2.795 \text{ V}$$

HW#5

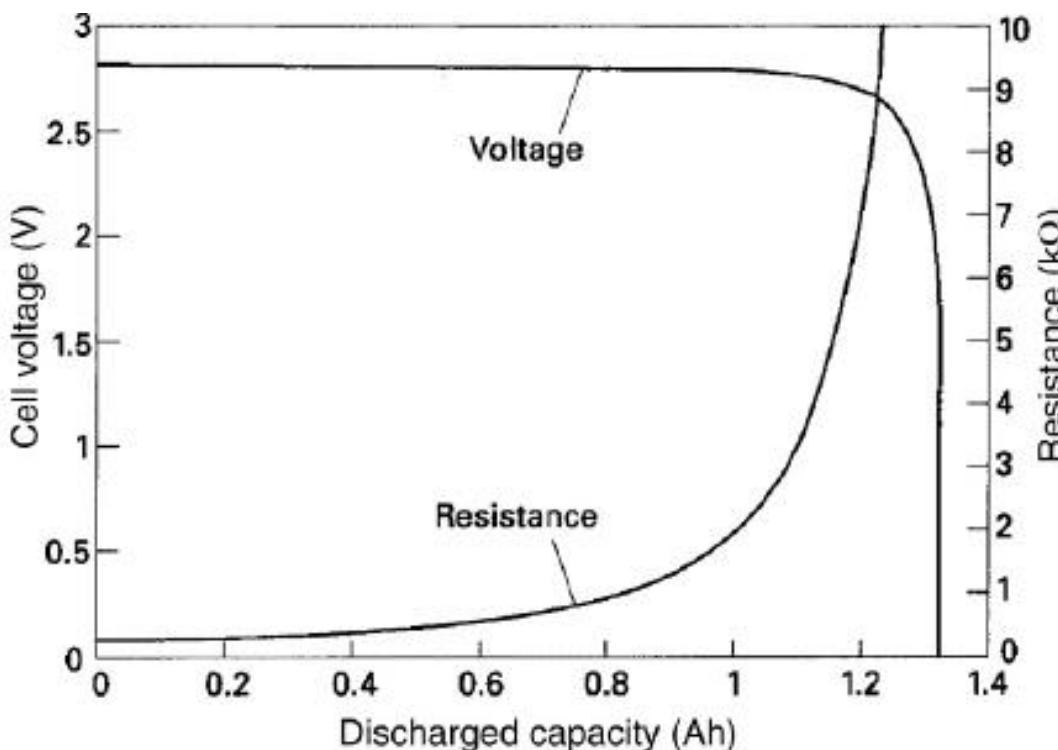


Fig. 2.2 Output voltage and internal resistance of a typical Li/I₂ battery of the type used in cardiac pacemakers

- Reaction↑→ LiI thickness (solid electrolyte)↑
- “positive-electrode limited”: positive electrode capacity is less than negative electrode capacity; this is the part of the cell that determines overall capacity

2.1 Calculation of the maximum theoretical specific energy

$$\text{MTSE (Wh/kg)} = 26805(xE/Wt) = 559.77 \text{ Wh/kg} \quad \text{HW\#5}$$

cf. 15 times Pb-acid cell

disadvantages: rechargeability, cost, discharge rate

2.2 Temperature dependence of the cell voltage

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

$$d(\Delta G_r)/dT = -\Delta S_r \quad \text{and} \quad dE/dT = \Delta S_r/z_r F$$

ΔS for the formation of LiI is given by

$$\begin{aligned}\Delta S_r(LiI) &= S(LiI) - S(Li) - 1/2S(I_2) \\ &= -1.38 \text{ J/K}\cdot\text{mol} \quad \text{HW\#5}\end{aligned}$$

→ cell voltage varies only slightly: $-1.43 \times 10^{-5} \text{ V/K}$

Table 2.1 Entropy data for some species at 25 and 225°C [3]

Species	S (25°C) J/K mol
Li	29.08
Zn	41.63
H ₂	130.68
O ₂	205.15
Cl ₂	304.32
I ₂	116.14
LiF	35.66
LiCl	59.30
LiBr	74.06
LiI	85.77
H ₂ O (liquid)	69.95
ZnO	43.64
Species	S (225°C) J/K mol
H ₂	145.74
O ₂	220.69
H ₂ O (gas)	206.66

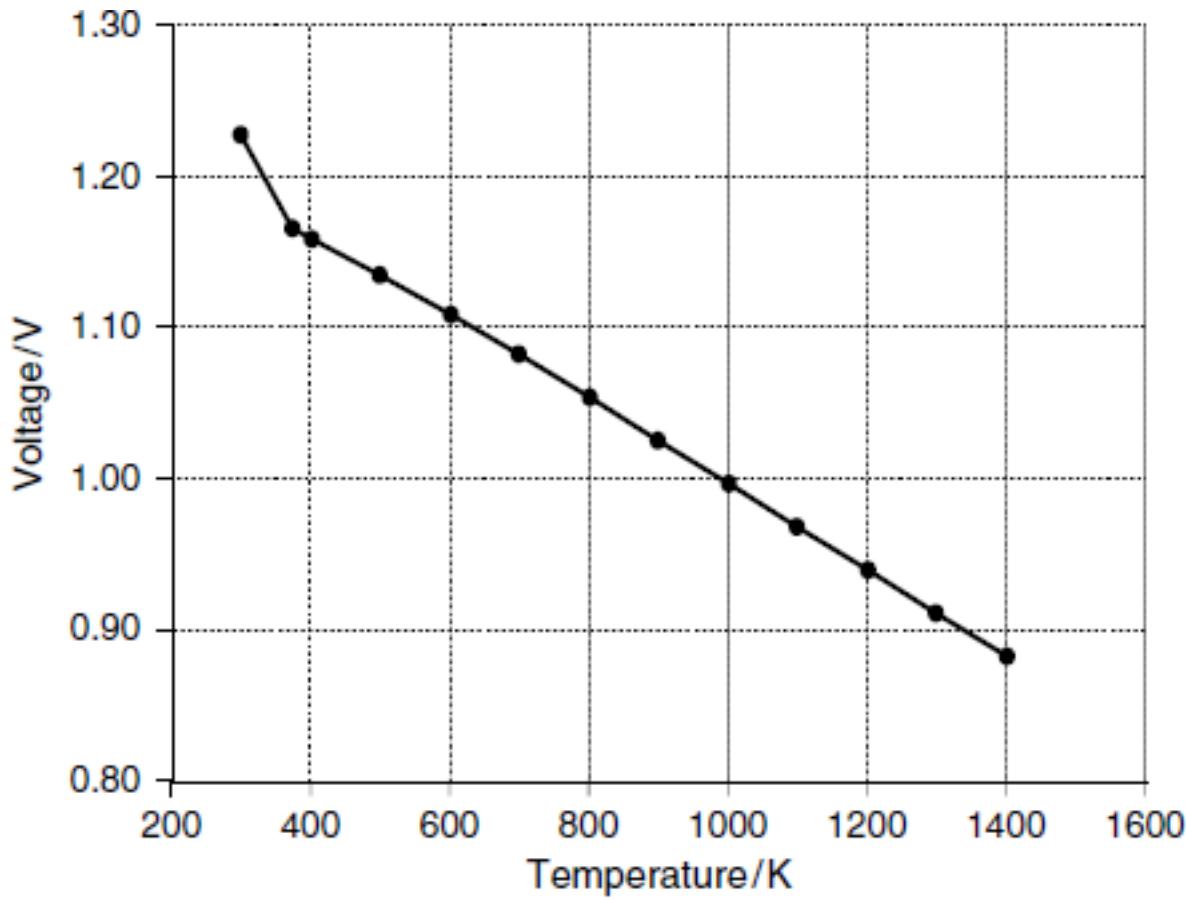


Fig. 2.3 Theoretic open circuit voltage of a H_2/O_2 fuel cell as a function of absolute temperature

-Zn/ O_2 battery that is commonly used in hearing aids,
where it is -5.2×10^{-4} V/K

- H_2/O_2 fuel cell where the voltage varies -1.7×10^{-3} V/K

3. The shape of discharge curves and the Gibbs phase rule

-3 types of discharge curves: flat, one-flat portion,
S-shape(large slope)

e.g. Li/I₂ cell (Fig.2.2): 1st type

-Why is flat in Li/I₂ cell? To understand the types → **Gibbs phase rule**

$$F = C - P + 2$$

C : the number of components (e.g. elements) present,

P : the number of phases present in this materials system

F : the number of degrees of freedom; i.e., the number of intensive thermodynamic parameters (pressure, temp, chemical potential or chemical composition)

-Li/I₂ cell: (-)electrode: only one phase Li, P = 1, C = 1, F = 2

F = 2 (temp, pressure) → no other freedom left → chemical as well as electrical potential have fixed value

The amount of Li in (-) electrode \downarrow as cell discharged and LiI produced \rightarrow since $F = 2$, if T & P are constant \rightarrow $F = 0 \rightarrow$ electrical potential of lithium electrode is independent of the state of charge of the cell

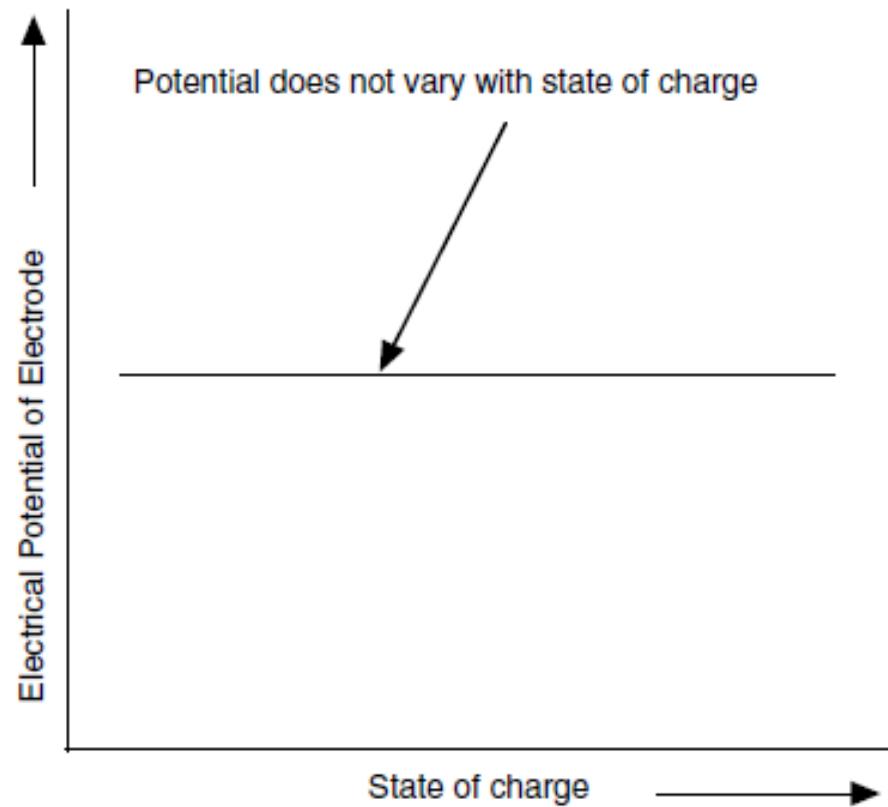


Fig. 2.4 Potential of a pure lithium electrode does not vary with the state of charge of the LiI cell

If some iodide could dissolve in lithium, forming a solid solution, which it does not (actually not happened) $\rightarrow C = 2$, $P = 1$, $F = 3 \rightarrow$ if T , P const, $F = 1 \rightarrow$ electrical potential varies

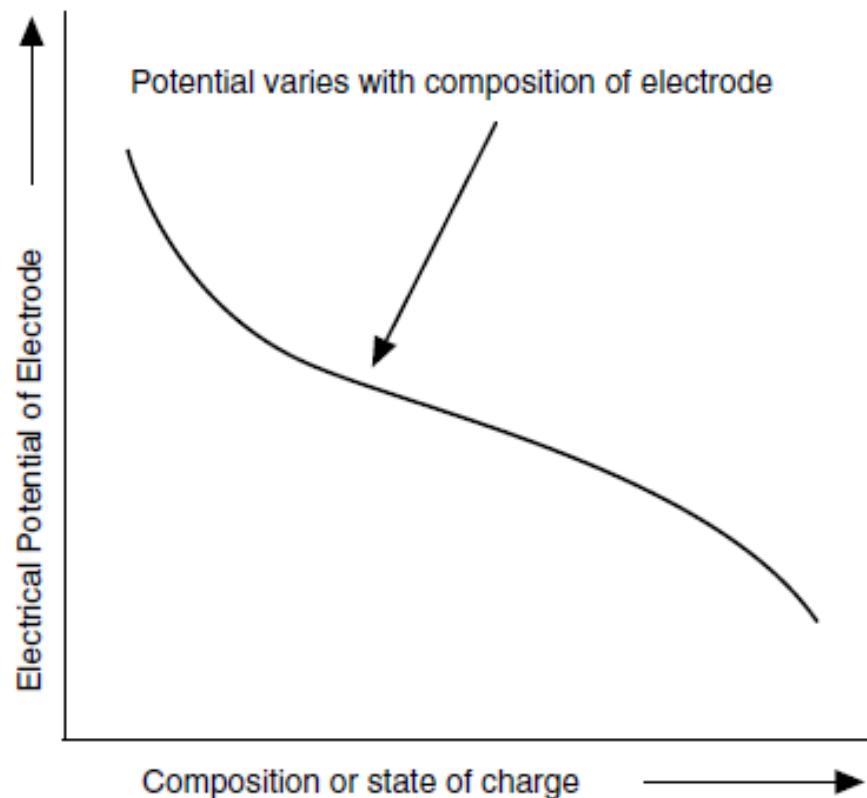


Fig. 2.5 Schematic representation of the variation of the electrical potential of an electrode as a function of its composition for the case in which the residual value of F is not zero

-positive electrode, one component, iodide C = 1, P =1, F =2
(same as negative electrode) → F = 0 for T & P const

(-), (+) both same: full cell (Fig.2.2)

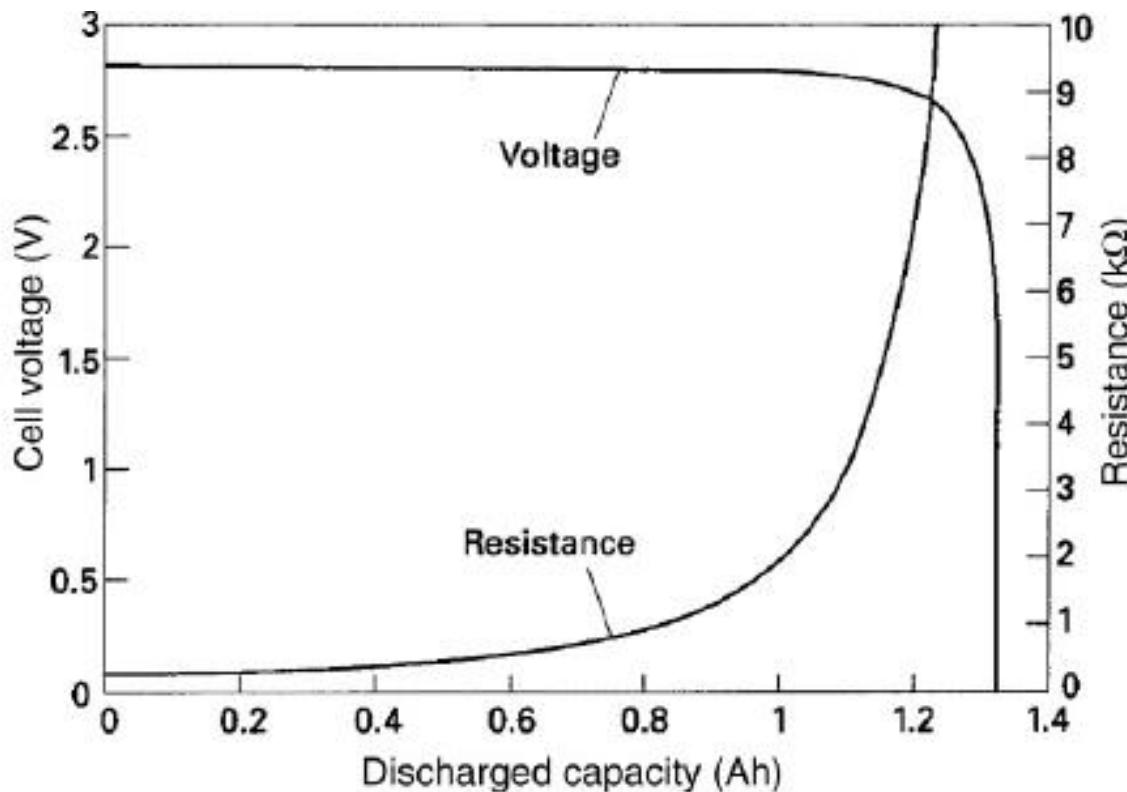


Fig. 2.2 Output voltage and internal resistance of a typical Li/I₂ battery of the type used in cardiac pacemakers

-chemical potential of the iodine electrode

$$\mu(I_2) = \mu^\circ(I_2) + RT \ln a(I_2)$$

for pure I_2 ,

$$\mu(I_2) = \mu^\circ(I_2)$$

-Now consider the voltage of the LiI_2 cell

$$E = -\Delta\mu(I_2)/z_i F$$

z_i is -2. activity of iodine at the positive side is unity

For Li, $E = -\Delta\mu(\text{Li})/z_i F$

z_i is +1. activity of lithium at the negative side is unity

-The shape of discharge curve is the result of the charge of both electrodes

e.g. multi-phase reactions in which residual $F = 0 \rightarrow$ set of constant voltage plateaus

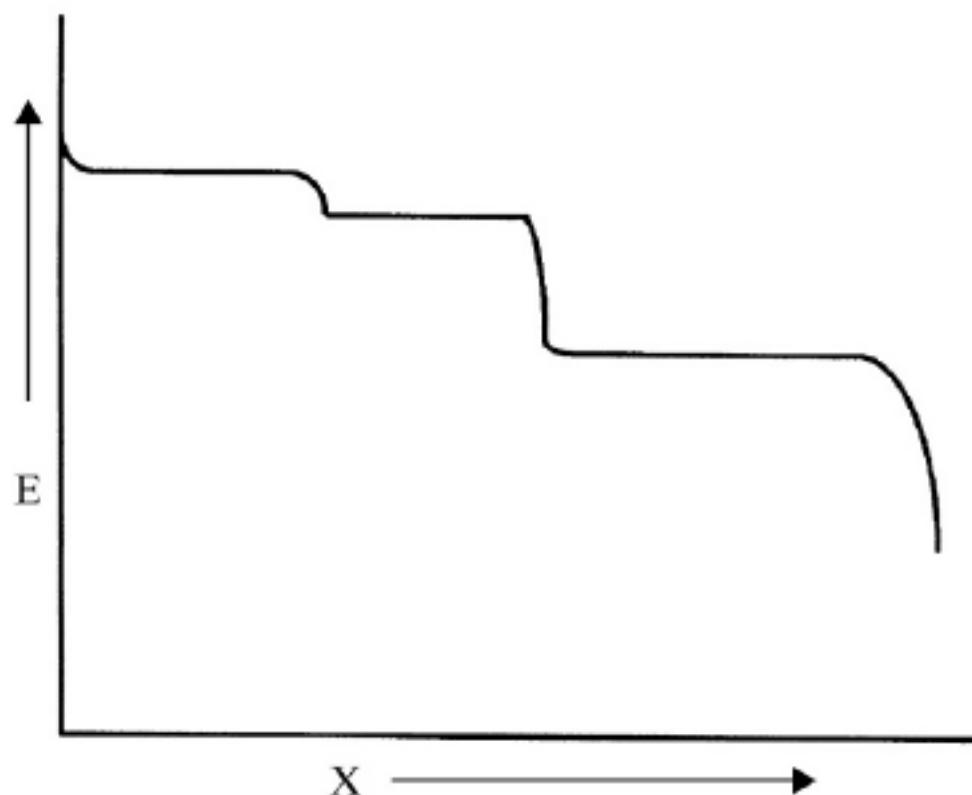


Fig. 2.6 Schematic equilibrium discharge curve of an electrode that undergoes a series of multi-phase reactions in which the residual value of F is zero

e.g. sequential reactions that are not similar

Li with Li-Ti-O spinel systems → 1 Li/mol inserted in the host spinel phase as a solid solution rxn → the potential varies continuously as a function of composition, $F = 2 - 1 + 2 = 3$ → additional Li causes nucleation, subsequent growth of a second phase with rocksalt structure, 2 Li/mol composition, $F = 2 - 2 + 2 = 2$

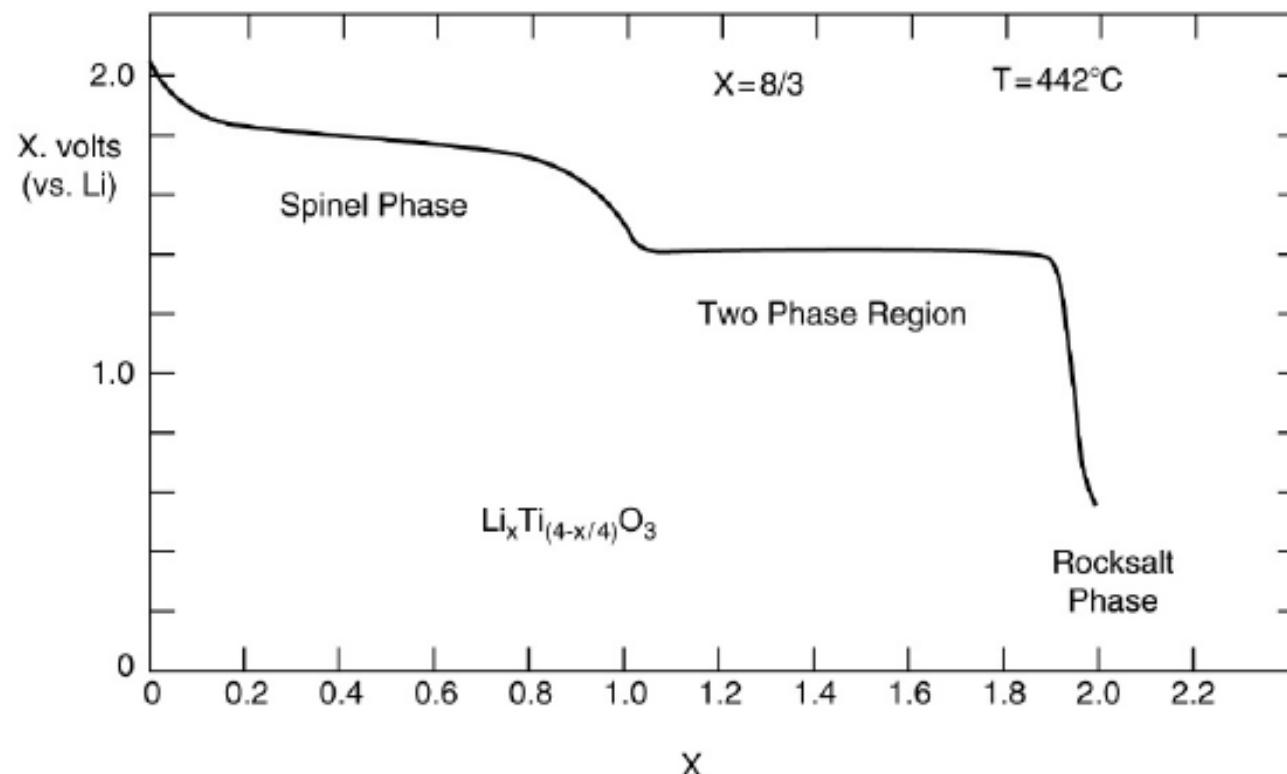


Fig. 2.7 Equilibrium discharge curve of a material in the Li-Ti-O system that initially had a composition with a spinel type of crystal structure

Insertion reaction up to 1 Li/mol → reconstitution reaction
(formation or displacement) takes place when more than one lithium is added → two regions within the material with different Li contents

$\text{Li} \uparrow \rightarrow$ interface movement

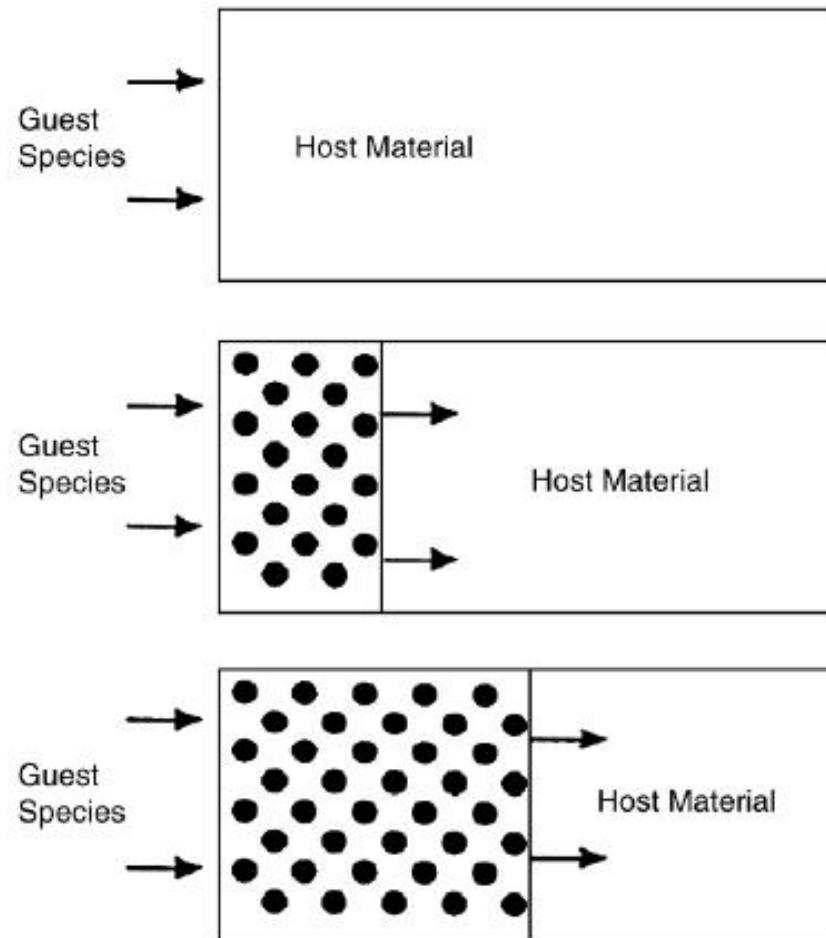


Fig. 2.8 A schematic representation of a one-dimensional moving interface reaction

Example of a series of reactions: Li-Mn-O system → three different reactions, two phase plateau, a single-phase solid solution region followed another two phase plateau

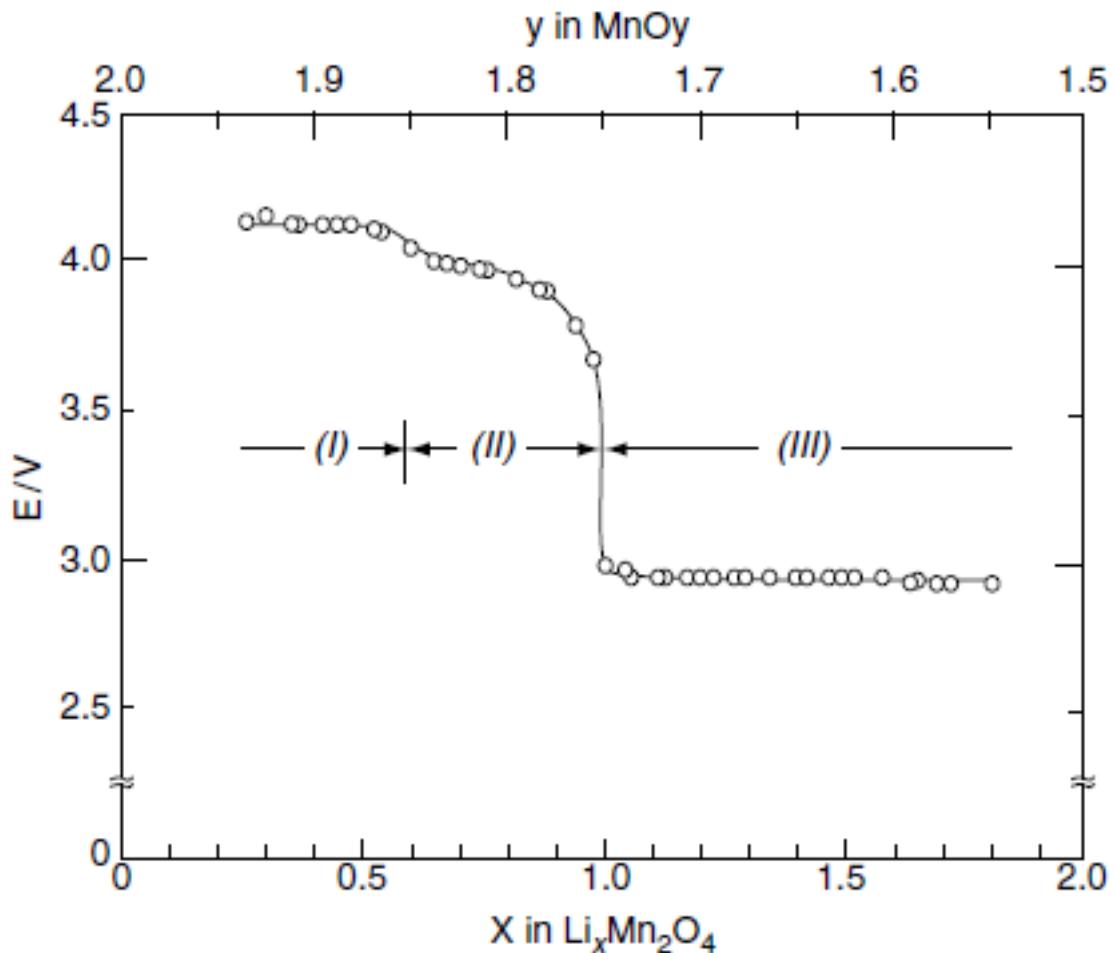


Fig. 2.9 Equilibrium discharge curve for $\text{Li}_x\text{Mn}_2\text{O}_4$

Experimentally confirmed by XRD

lattice parameters remain constant within two-phase regions, and vary with the composition within the single-phase solid solution region

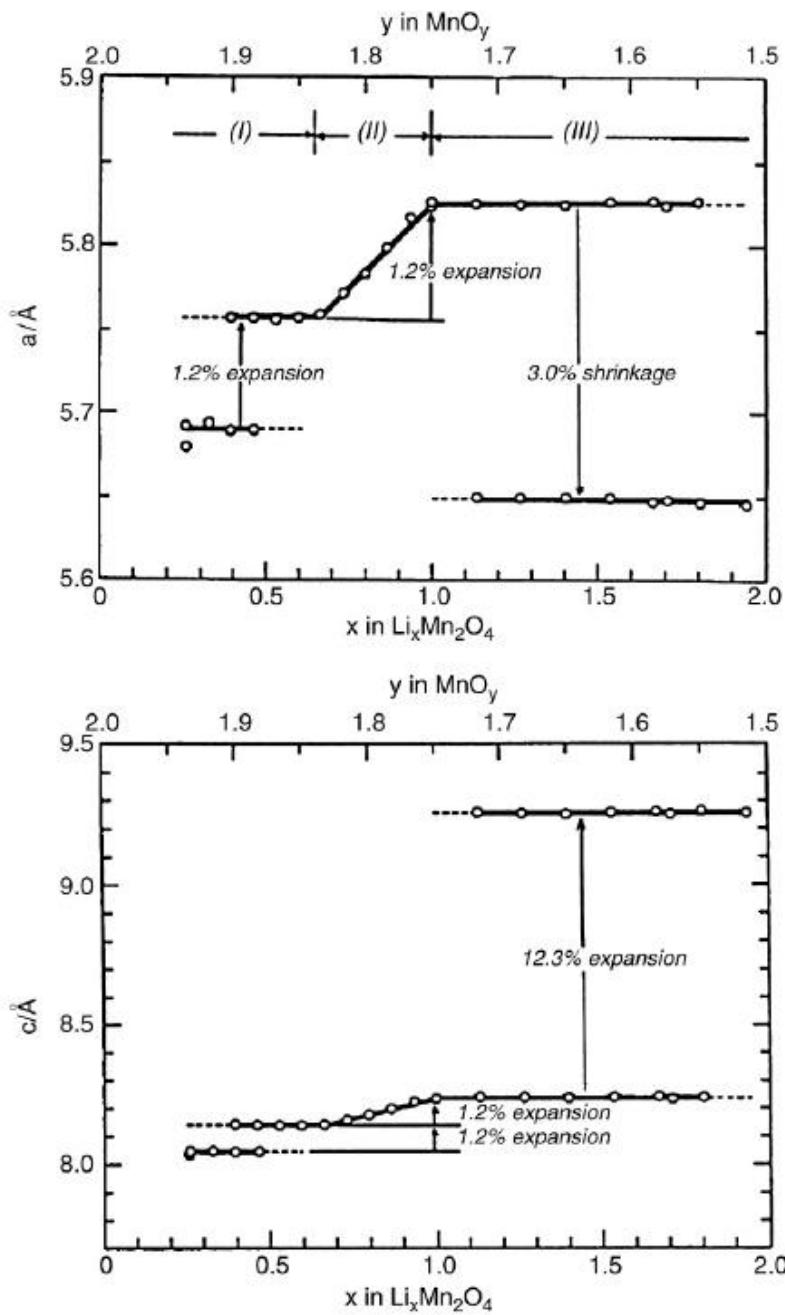


Fig. 2.10 Changes in unit cell dimensions as a function of composition in $\text{Li}_x\text{Mn}_2\text{O}_4$

4. The Coulometric titration technique

- Electrochemical measurement to obtain thermodynamic information
- Consider electrochemical cell to investigate phase A_yB
 $A / \text{electrolyte}(A^+ \text{ ion}) / A_yB$

Assume pure A ($a(A) = 1$), isobaric(const P), isothermal(const T) condition

→ OCV E is a direct measure of chemical potential and activity A in phase A_yB according to

$$E = -\Delta\mu_A/z_{A^+}F = -(RT/z_{A^+}F) \ln a(A)$$

where $z_{A^+} = 1$

-If a positive current is passed through the cell using an electronic source, A^+ ions are transported through the electrolyte from the left electrode to the right electrode → y in the A_yB phase is increased.

-When a steady value of current I is applied for a fixed time t , the amount of charge Q that is passed across the cell is

$$Q = It$$

-Number of moles of species A which is transported during this current pulse is

$$\Delta m(A) = Q/z_{A+}F$$

so that change in the value of y , the mole fraction of species A, is

$$\Delta y = \Delta m(A)/m(B) = Q/(z_{A+}Fm(B))$$

where $m(B)$ is the number of moles of B present in the electrode

e.g.