

## 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,  $\Delta\mu_i = \Delta G_j$

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

$z_i$ : 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  $\mu_i^\circ$ : 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

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

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

## 2. A Simple Example: The Lithium/Iodine Cell

- A lithium/iodine (Li/I<sub>2</sub>) 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 Lil as a solid electrolyte

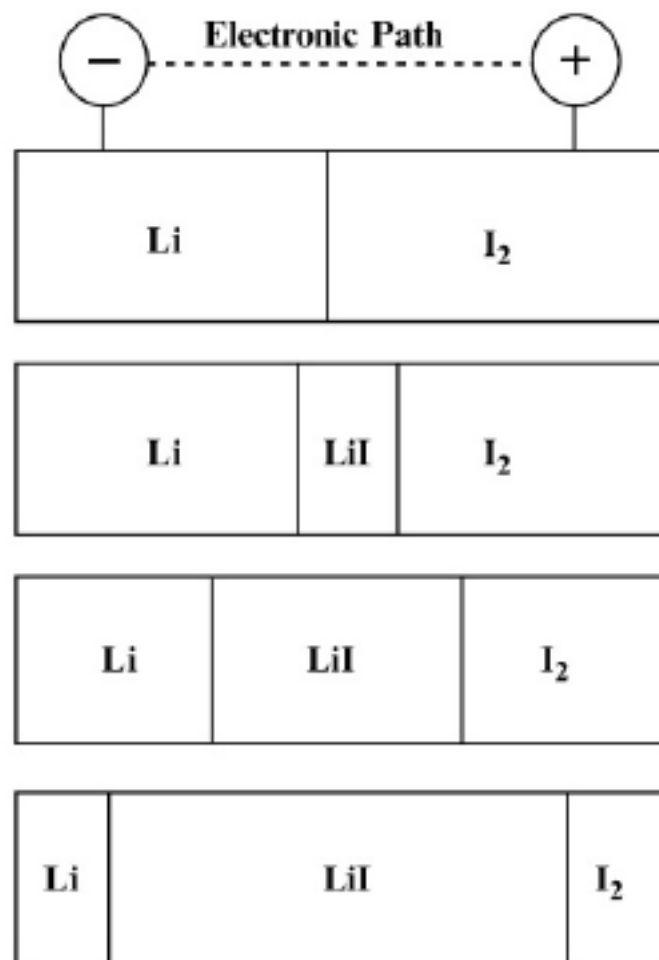


Virtual reaction (가상반응),  $\text{Li} + \frac{1}{2}\text{I}_2 \rightarrow \text{LiI}$

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

where

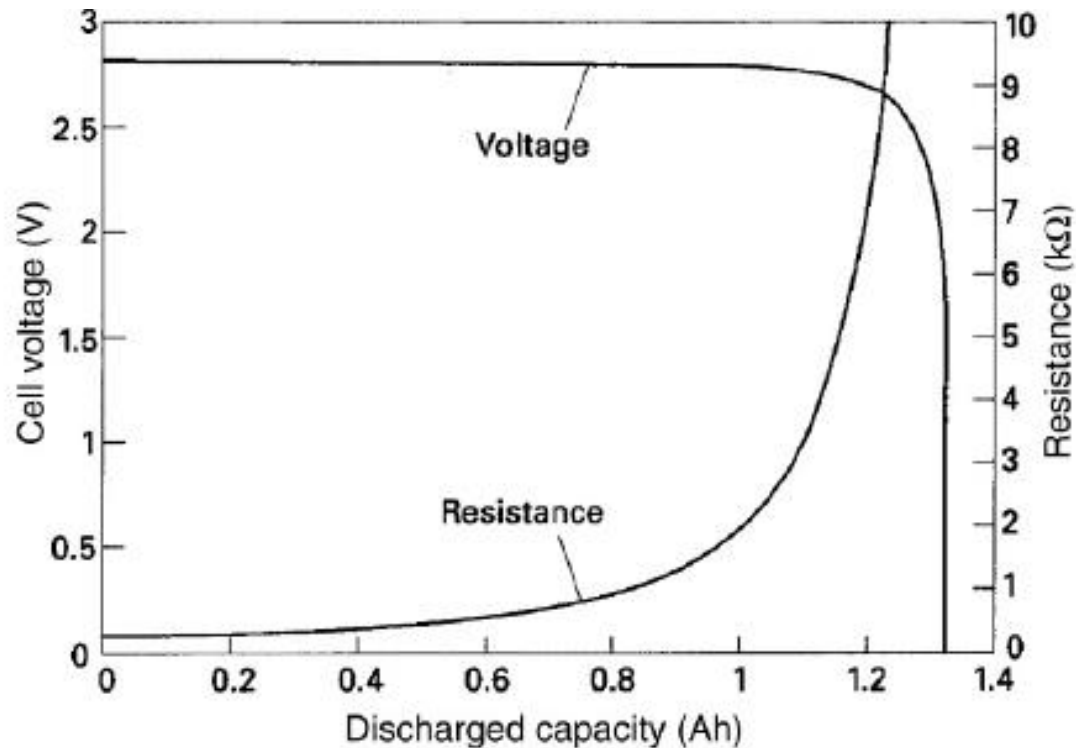
$$\Delta G_r = \Delta G_f(\text{LiI}) \text{ and } z_i \text{ is } +1 \text{ for } \text{Li}^+$$



**Fig. 2.1** Schematic representation of the microstructure of a Li/I<sub>2</sub> cell at several stages of discharge

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

HW#5



**Fig. 2.2** Output voltage and internal resistance of a typical Li/I<sub>2</sub> battery of the type used in cardiac pacemakers

- Reaction  $\uparrow \rightarrow$  LiI thickness (solid electrolyte)  $\uparrow$
- “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

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

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

$\Delta S$  for the formation of LiI is given by

$$\begin{aligned} \Delta S_r(\text{LiI}) &= S(\text{LiI}) - S(\text{Li}) - 1/2 S(\text{I}_2) \\ &= -1.38 \text{ J/K}\cdot\text{mol} \end{aligned}$$

HW\#5

→ 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 <sub>2</sub>	130.68
O <sub>2</sub>	205.15
Cl <sub>2</sub>	304.32
I <sub>2</sub>	116.14
LiF	35.66
LiCl	59.30
LiBr	74.06
LiI	85.77
H <sub>2</sub> O (liquid)	69.95
ZnO	43.64
Species	$S$ (225°C) J/K mol
H <sub>2</sub>	145.74
O <sub>2</sub>	220.69
H <sub>2</sub> O (gas)	206.66



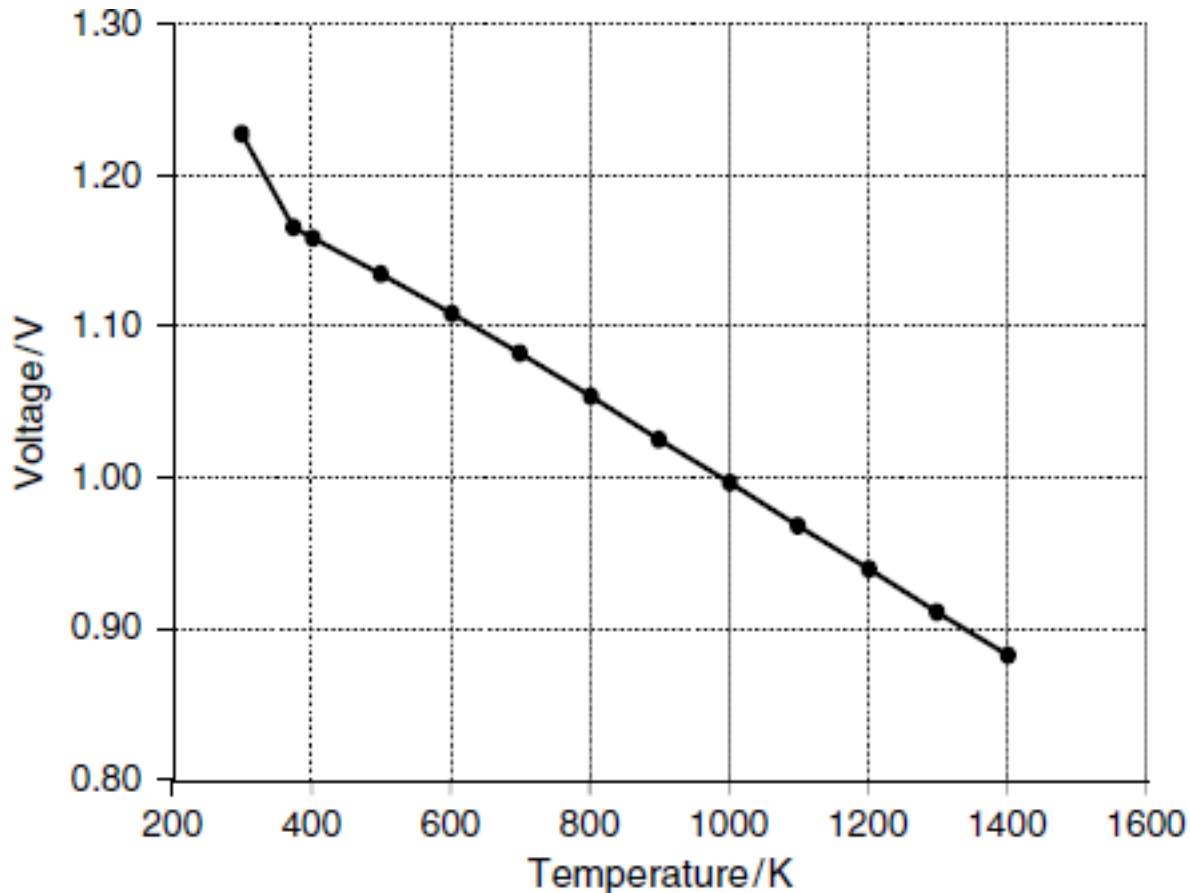


Fig. 2.3 Theoretic open circuit voltage of a H<sub>2</sub>/O<sub>2</sub> fuel cell as a function of absolute temperature

-Zn/O<sub>2</sub> battery that is commonly used in hearing aids,  
 where it is  $-5.2 \times 10^{-4}$  V/K

-H<sub>2</sub>/O<sub>2</sub> fuel cell where the voltage varies  $-1.7 \times 10^{-3}$  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/I<sub>2</sub> cell (Fig.2.2): 1<sup>st</sup> type

-Why is flat in Li/I<sub>2</sub> 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/I<sub>2</sub> 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 ↓ as cell discharged and LiI produced → since  $F = 2$ , if T & P are constant →  $F = 0$  → electrical potential of lithium electrode is independent of the state of charge of the cell

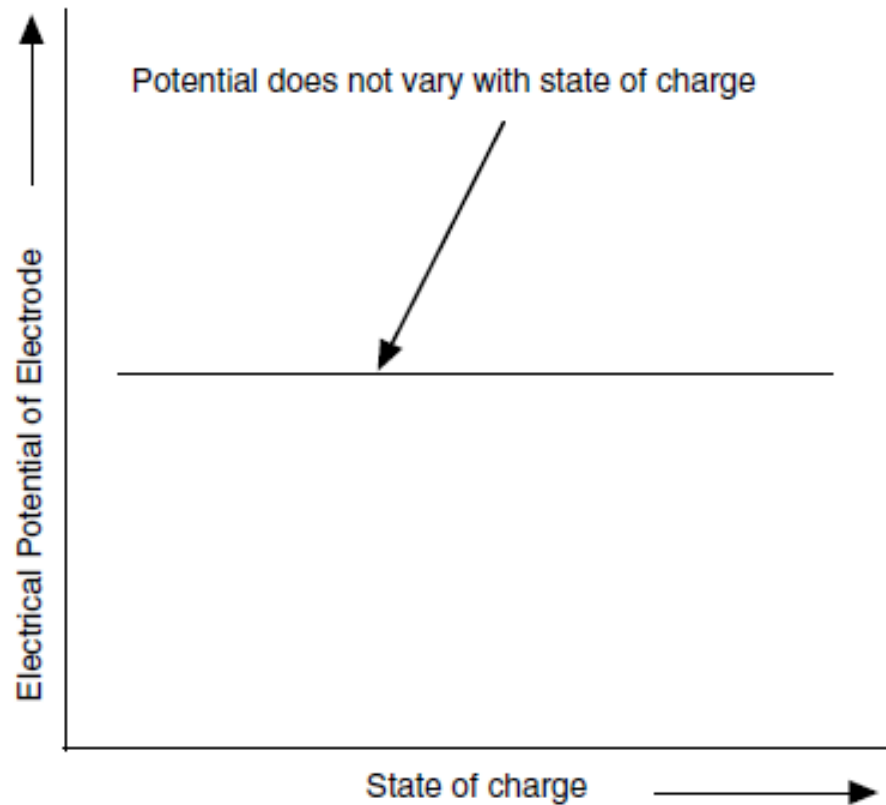
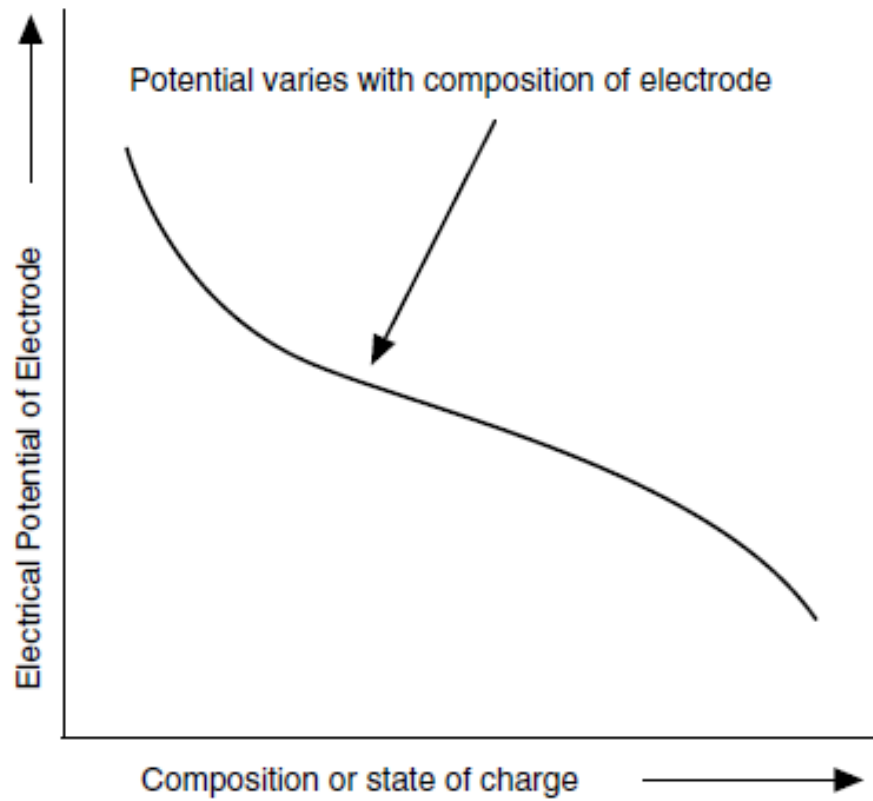


Fig. 2.4 Potential of a pure lithium electrode does not vary with the state of charge of the LiI cell

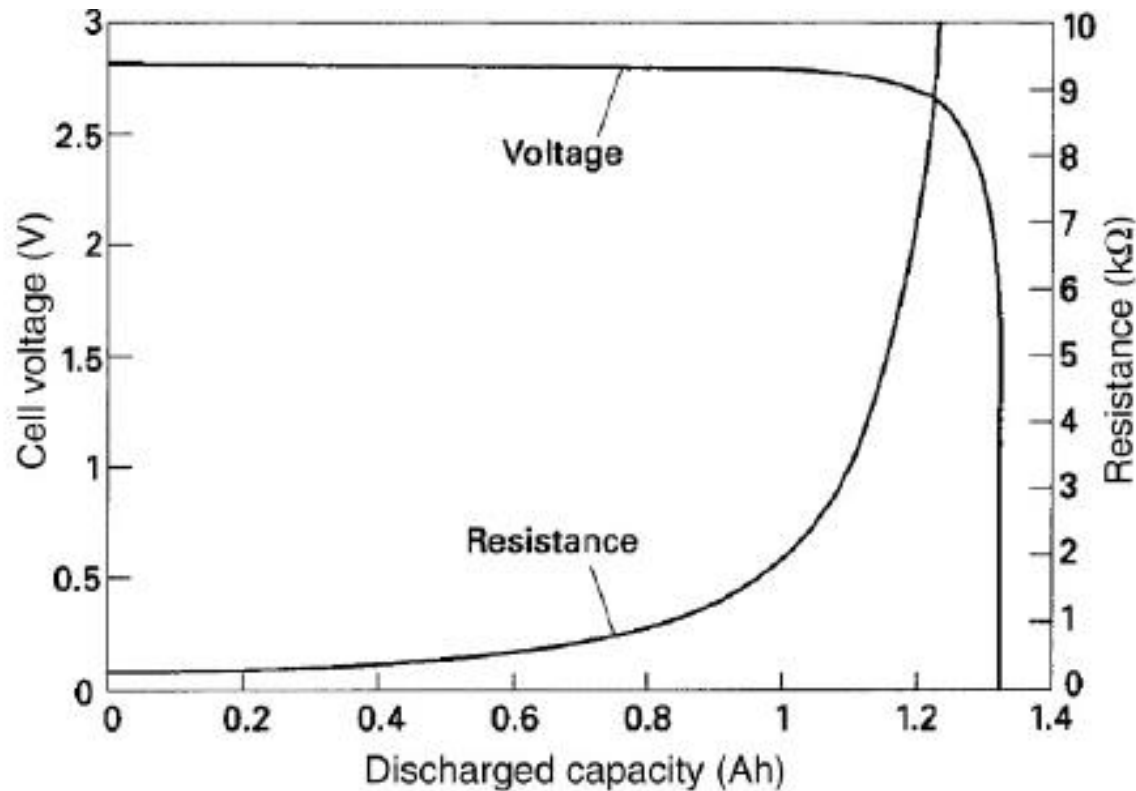
If some iodide could dissolve in lithium, forming a solid solution, which it does not (actually not happened)  $\rightarrow C = 2, P = 1, F = 3 \rightarrow$  if  $T, P$  const,  $F = 1 \rightarrow$  electrical potential varies



**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)  $\rightarrow F = 0$  for  $T$  &  $P$  const

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



**Fig. 2.2** Output voltage and internal resistance of a typical  $\text{Li}/\text{I}_2$  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  $Li/I_2$  cell

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

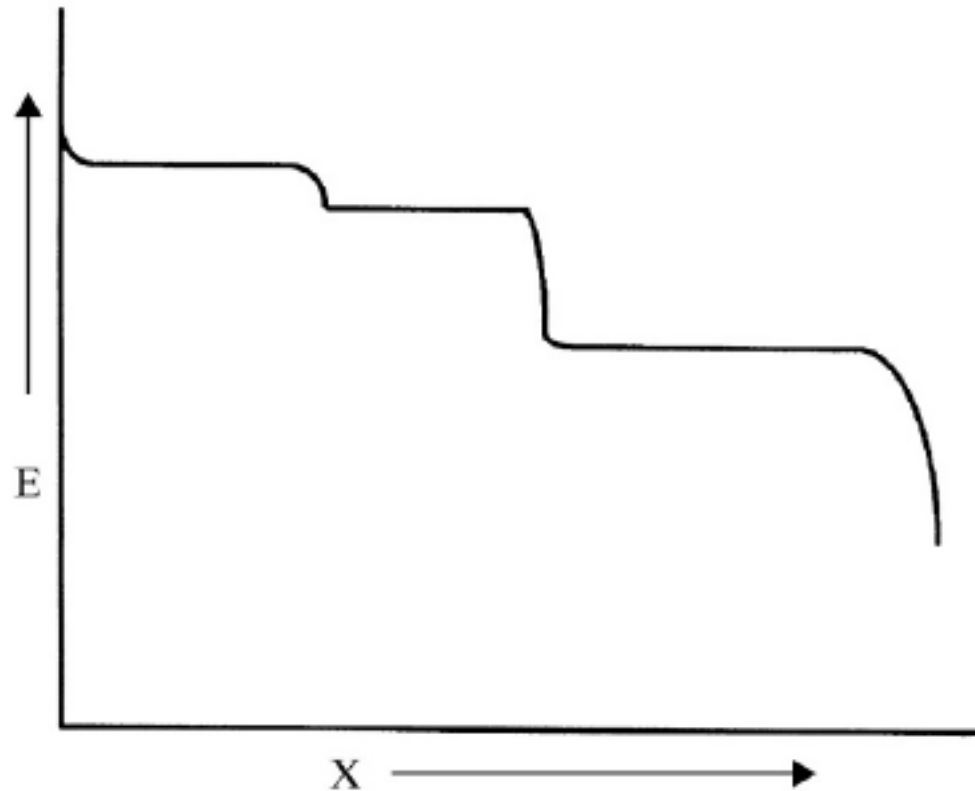
$z_i$  is -2. activity of iodine at the positive side is unity

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

$z_i$  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

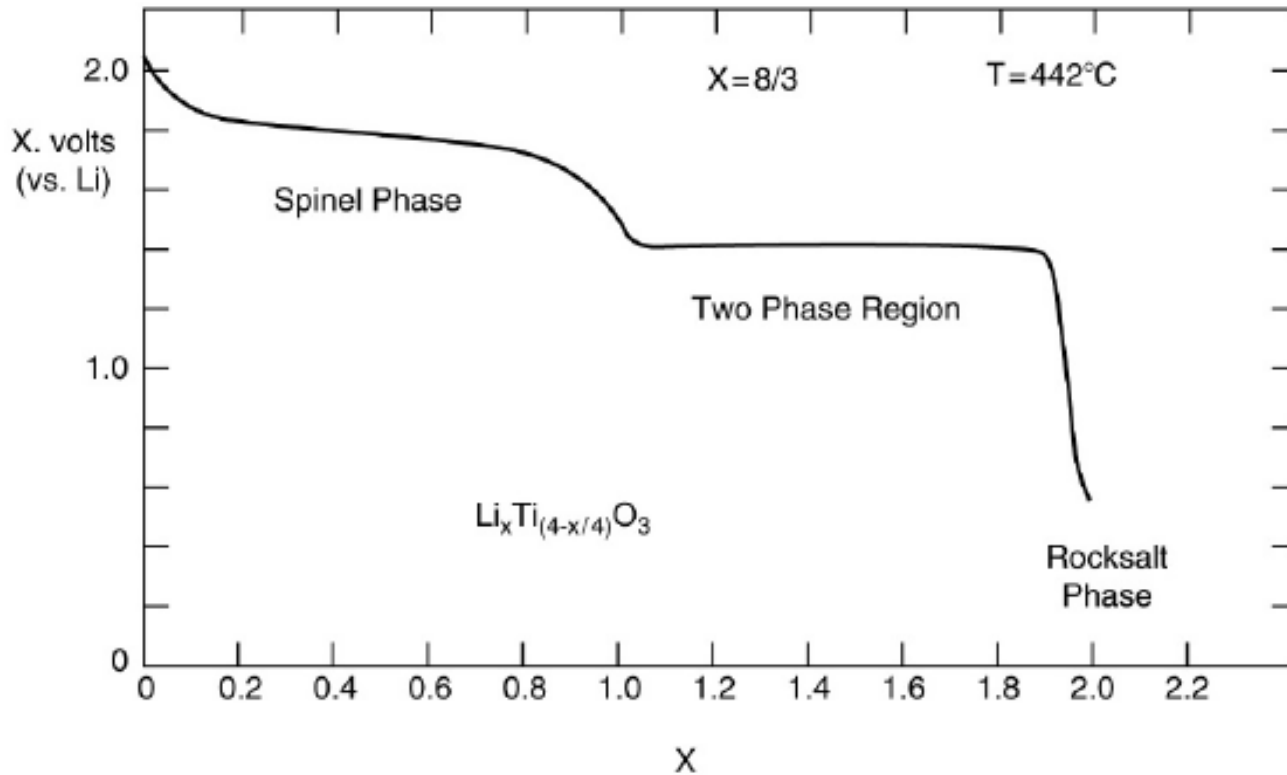
e.g. multi-phase reactions in which residual  $F = 0 \rightarrow$  set of constant voltage plateaus



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

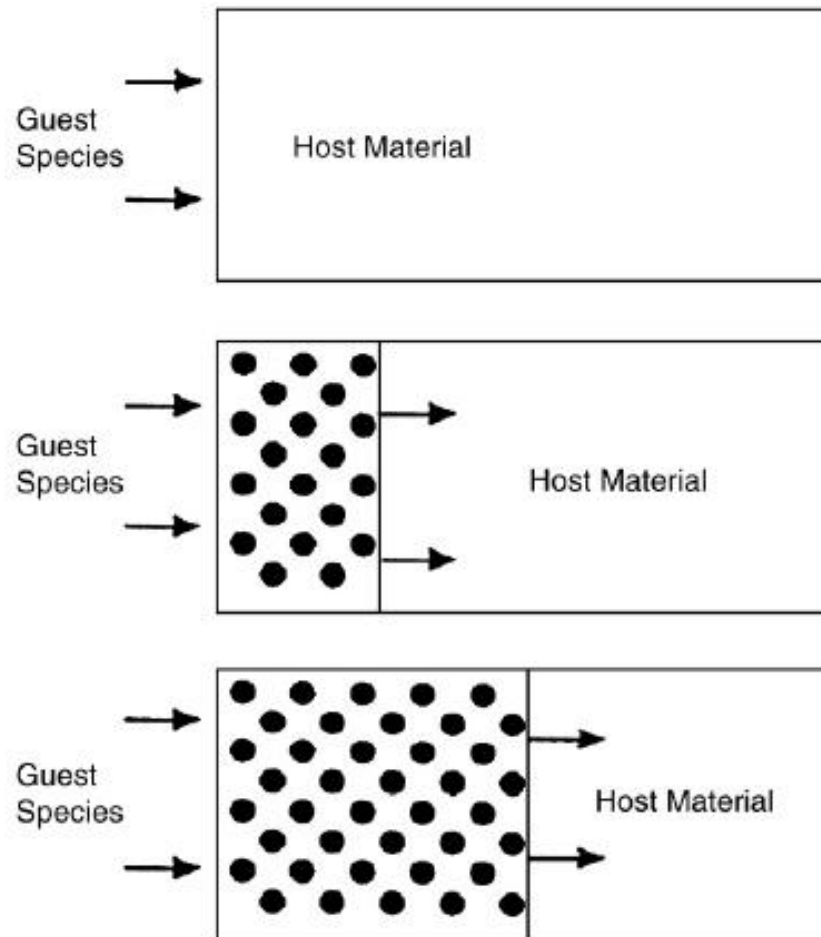


**Fig. 2.7** Equilibrium discharge curve of a material in the Li-Ti-O system that initially had a composition with a spinel type of crystal structure



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

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  $\rightarrow$  three different reactions, two phase plateau, a single-phase solid solution region followed another two phase plateau

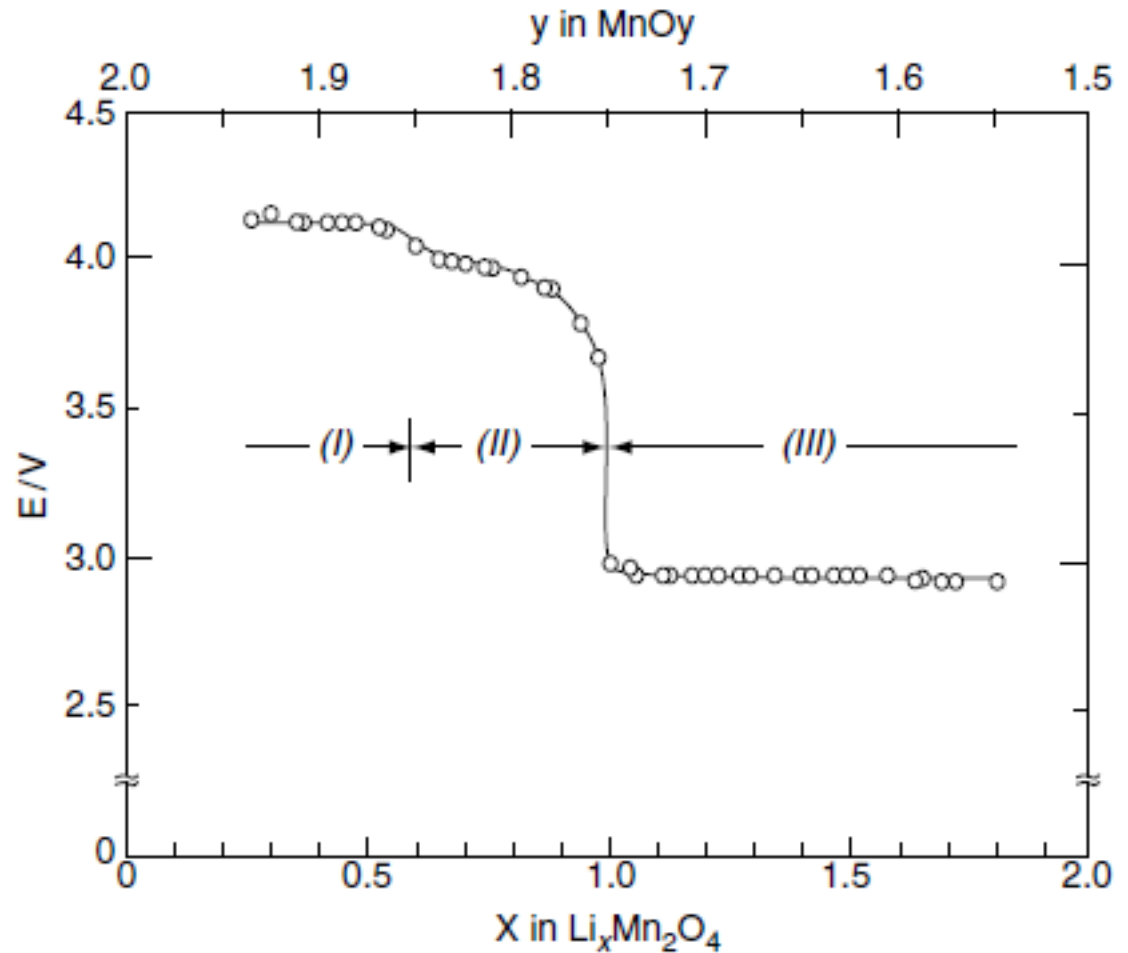


Fig. 2.9 Equilibrium discharge curve for  $\text{Li}_x\text{Mn}_2\text{O}_4$

Experimentally confirmed by XRD

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

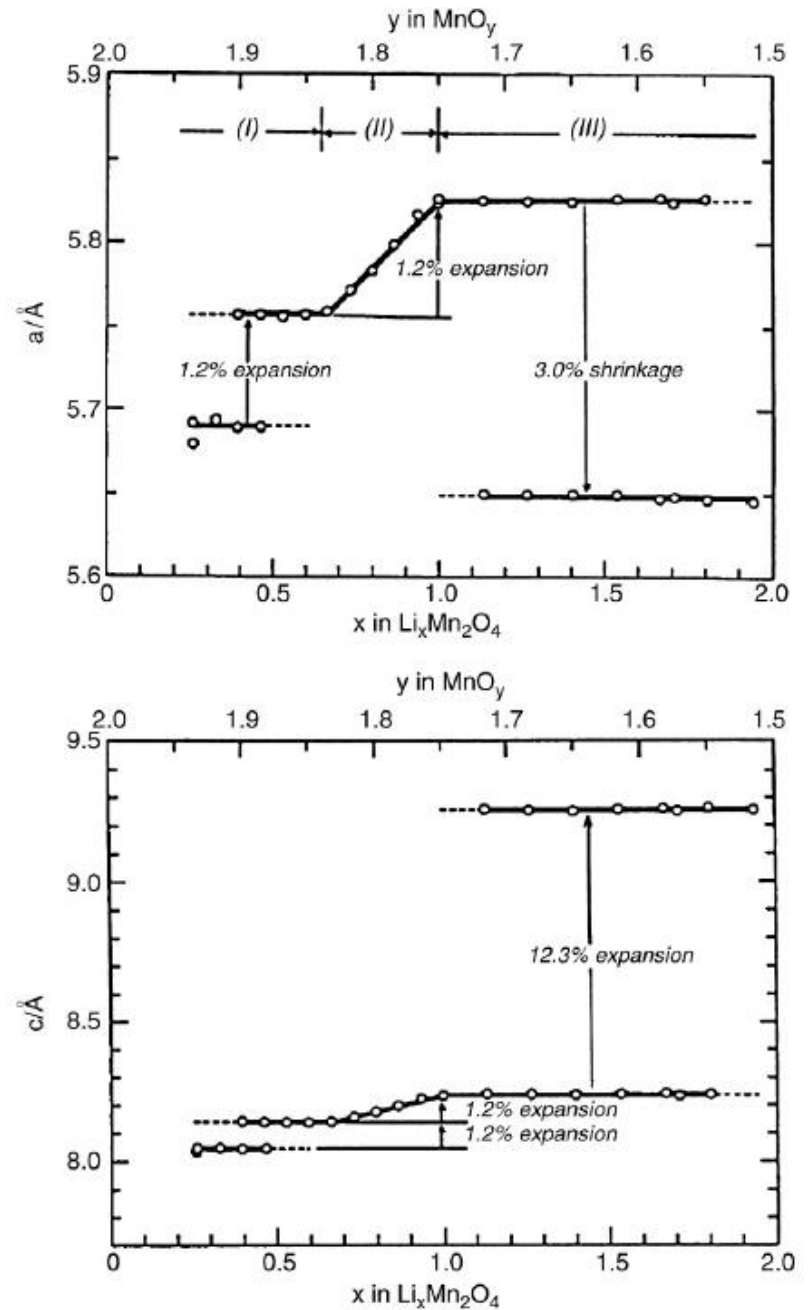


Fig. 2.10 Changes in unit cell dimensions as a function of composition in  $\text{Li}_x\text{Mn}_2\text{O}_4$

## 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.