

Battery Fundamentals

1. Components of a cell
2. Classification of batteries
3. Theoretical capacity and state of charge
4. Cell characteristics and electrochemical performance
5. Ragone plots
6. Heat generation
7. Efficiency of secondary cells
8. Charge retention and self-discharge
9. Capacity fade in secondary cells

Components of a cell

-Components of Daniel cell (1839)

Negative electrode: zinc bar

Positive electrode: copper bar

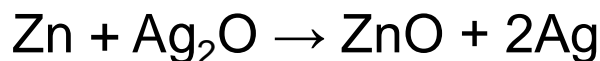
Electrolyte: ionic conductor, electronic insulator

Separator

$$E = E^0 - (RT/2F)\ln(a_{Zn^{2+}}/a_{Cu^{2+}})$$

$$E^0 = E_{Cu}^0 - E_{Zn}^0 = 0.337 - (-0.763) = 1.10 \text{ V}$$

-A commercial cell: silver-zinc coin or button cell



$$E^0 = -\Delta G/nF$$

$$= [-11210 - (-318300)]/[(2)96485] = 1.591 \text{ V}$$

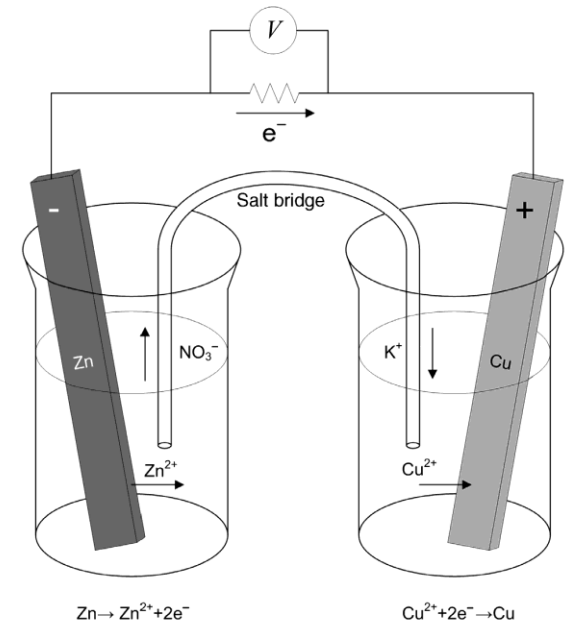
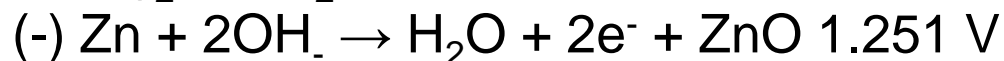
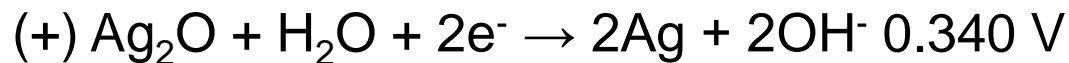


Figure 7.1 The Daniell cell is a simple battery, shown undergoing discharge.

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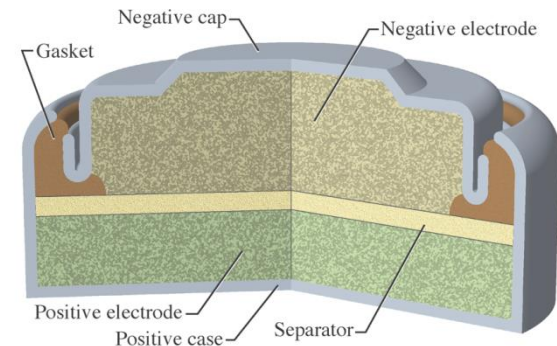


Figure 7.2 Silver-zinc coin cell.

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Classification of batteries & cell chemistries

-Primary(1차) or secondary(2차, rechargeable)

Primary battery: higher specific energy(Wh/kg) & power (W/kg)

Special category of primary battery: reserve battery

-Two important classes of electrode reactions for batteries

1. Reconstruction (or conversion reaction): formation or displacement

(i) $A + B \rightarrow AB$ formation (생성)

e.g. $2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$ ($\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$, $2\text{Li}^+ + 2\text{SO}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{S}_2\text{O}_4$)

(ii) $A + \text{BX} \rightarrow \text{AX} + \text{B}$ displacement (치환)

e.g. $\text{Zn} + \text{Ag}_2\text{O} \rightarrow \text{ZnO} + 2\text{Ag}$

-dissolution-precipitation mechanism

$\text{M} \rightarrow \text{M}^{z+} + z\text{e}^-$ dissolution

$\text{M}^{z+} + z\text{X}^- \rightarrow \text{MX}_z(\text{s})$ precipitation

Secondary battery: galvanic cell + electrolytic cell

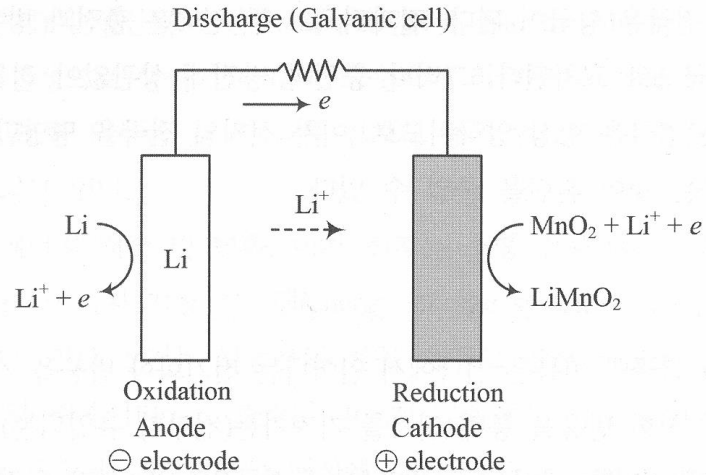


그림 1-21 Li/MnO₂ 이차 전지의 방전 과정에서 전극 반응과 전극의 명칭

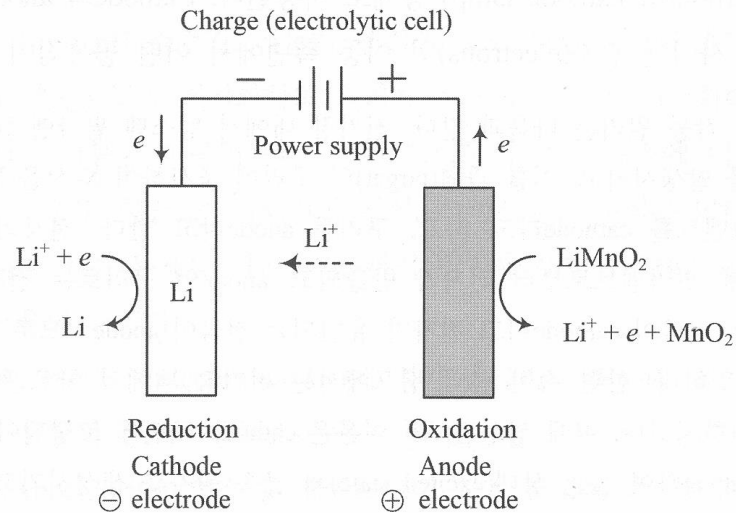


그림 1-22 Li/MnO₂ 이차 전지의 충전 과정에서 전극 반응과 전극의 명칭

Table 7.1 Example Chemistries for a Number of Common Batteries

Cell	Electrochemical reactions	Nominal Cell potential	Comments
Lead-acid	$\text{Pb(s)} + \text{HSO}_4^- + \text{H}_2\text{O} \rightarrow \text{PbSO}_4(\text{s}) + \text{H}_3\text{O}^+ + 2\text{e}^-$ $\text{PbO}_2(\text{s}) + 3\text{H}_3\text{O}^+ + \text{HSO}_4^- + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l})$ $\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_3\text{O}^+ + 2\text{HSO}_4^- \rightarrow 2\text{PbSO}_4(\text{s}) + 4\text{H}_2\text{O}(\text{l})$	1.8 V	Secondary During discharge, lead sulfate is formed at both electrodes. The electrolyte is part of the active material
Alkaline	$\text{Zn(s)} + 2\text{OH}^- = \text{ZnO(s)} + \text{H}_2\text{O}(\text{l}) + 2\text{e}^-$ $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$ $\text{Zn(s)} + 2\text{MnO}_2(\text{s}) = \text{ZnO(s)} + \text{Mn}_2\text{O}_3$	1.5 V	Primary Common battery
Lithium-ion	$\text{Li}_x\text{C}_6 \rightarrow x\text{Li}^+ + xe^- + 6\text{C}$ $x\text{Li}^+ + xe^- + \text{Mn}_2\text{O}_4 \rightarrow \text{Li}_x\text{Mn}_2\text{O}_4$ $\text{Li}_x\text{C}_6 + \text{Mn}_2\text{O}_4 \rightarrow \text{Li}_x\text{Mn}_2\text{O}_4 + 6\text{C}$	3.5–4.2 V	Secondary The spinel manganese dioxide is just one of the chemistries of rechargeable lithium-ion batteries
Silver-zinc	$\text{Zn} + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + 2\text{e}^- + \text{ZnO}$ $\text{Ag}_2\text{O} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ag} + 2\text{OH}^-$ $\text{Zn} + \text{Ag}_2\text{O} \rightarrow \text{ZnO} + 2\text{Ag}$	1.5 V	Manufactured as both a primary and a secondary battery
Ni/Cd	$\text{Cd(s)} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2 + 2\text{e}^-$ $\text{NiOOH} + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + \text{OH}^-$ $\text{Cd(s)} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + \text{Ni(OH)}_2$	1.2 V	Secondary, out of favor because of environmental issue with cadmium
Ni/Fe	$\text{Fe} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 + 2\text{e}^-$ $\text{NiOOH} + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + \text{OH}^-$ $\text{Fe} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{Ni(OH)}_2$	1.2 V	Secondary, also called the Edison cell
NiMH	$\text{MH} + \text{OH}^- \rightarrow \text{M} + \text{H}_2\text{O} + \text{e}^-$ $\text{NiOOH} + \text{e}^- + \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 + \text{OH}^-$ $\text{MH} + \text{NiOOH} \rightarrow \text{M} + \text{Ni(OH)}_2$	1.2 V	Secondary
Na-S	$\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ $x\text{S} + 2\text{e}^- \rightarrow \text{S}_x^{2-}$ $2\text{Na} + x\text{S} \rightarrow \text{Na}_2\text{S}_x$	1.9 V	Secondary high temperature
Li-SO ₂	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ $2\text{Li}^+ + 2\text{SO}_2 + 2\text{e}^- \rightarrow \text{Li}_2\text{S}_2\text{O}_4$ $2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$	3 V	Primary Lithium-sulfur dioxide
Li-SOCl ₂	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ $2\text{SOCl}_2 + 4\text{e}^- \rightarrow 4\text{Cl}^- + \text{S} + \text{SO}_2$ $4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$	3.4 V	Primary Lithium thionyl chloride
Li/FeS ₂	$\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$ $4\text{Li}^+ + 4\text{e}^- + 3\text{FeS}_2 \rightarrow \text{Li}_4\text{Fe}_2\text{S}_5 + \text{FeS}$ $4\text{Li} + 3\text{FeS}_2 \rightarrow \text{Li}_4\text{Fe}_2\text{S}_5 + \text{FeS}$	1.5 V	Reserve Thermally activated LiCl/KCl eutectic for electrolyte
Mg/AgCl	$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ $2\text{AgCl} + 2\text{e}^- \rightarrow 2\text{Ag} + 2\text{Cl}^-$ $\text{Mg} + 2\text{AgCl} \rightarrow 2\text{Ag} + \text{MgCl}_2$	1.4 V	Reserve water activated

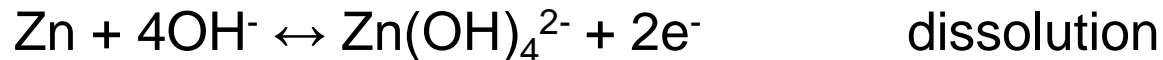
-The amount of precipitated depends on the solubility of MX_z in the solvent
 → three solubility conditions : (1) an insoluble salt, (2) a highly soluble salt,
 (3) an intermediate or sparingly soluble salt

(1) An insoluble salt: positive electrode of a lithium thionyl chloride battery



electrolyte: a mixture of $\text{LiAlCl}_4 + \text{SOCl}_2 \rightarrow$ insoluble → a primary battery

(2) A highly soluble salt: zinc electrode in an alkaline electrolyte(KOH)



ZnO soluble in KOH → a rechargeable battery

(3) A sparingly soluble: negative electrode of the lead-acid battery



Solubility is small enough so that during cycling cycle → a rechargeable battery possible

2. Insertion

-stable host material + guest material for unoccupied sites of the host material → the insertion into a layered structure of the host material, “**intercalation**” → retain crystalline structure of the host material → highly reversible

e.g. Li intercalation into a layered TiS_2 (van der Waals forces between the layer), “**galley space**”

A positive electrode for a lithium-ion cell



where x varies from zero to one

-this insertion process results in a kind of solid solution of the guest species in the host → a characteristic sloping discharge curve (Fig. 7.5)

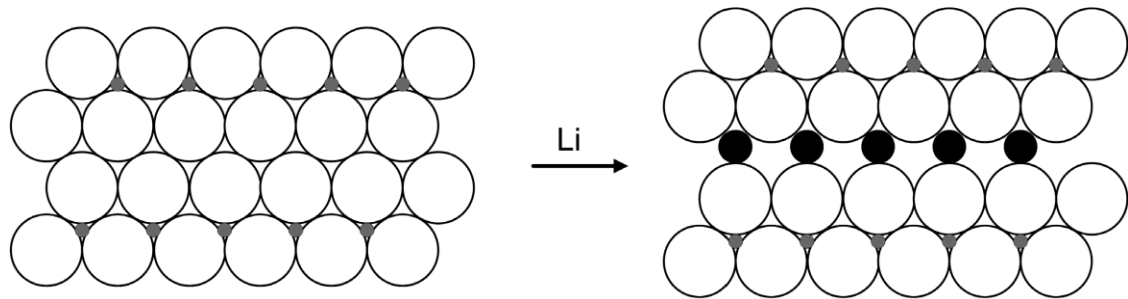
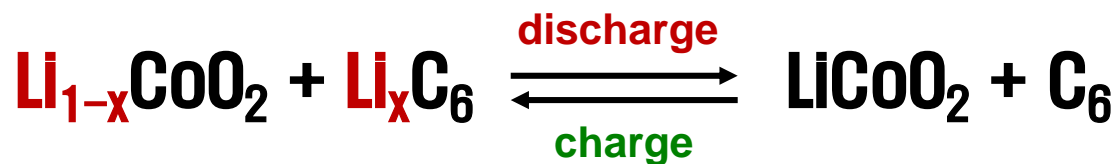
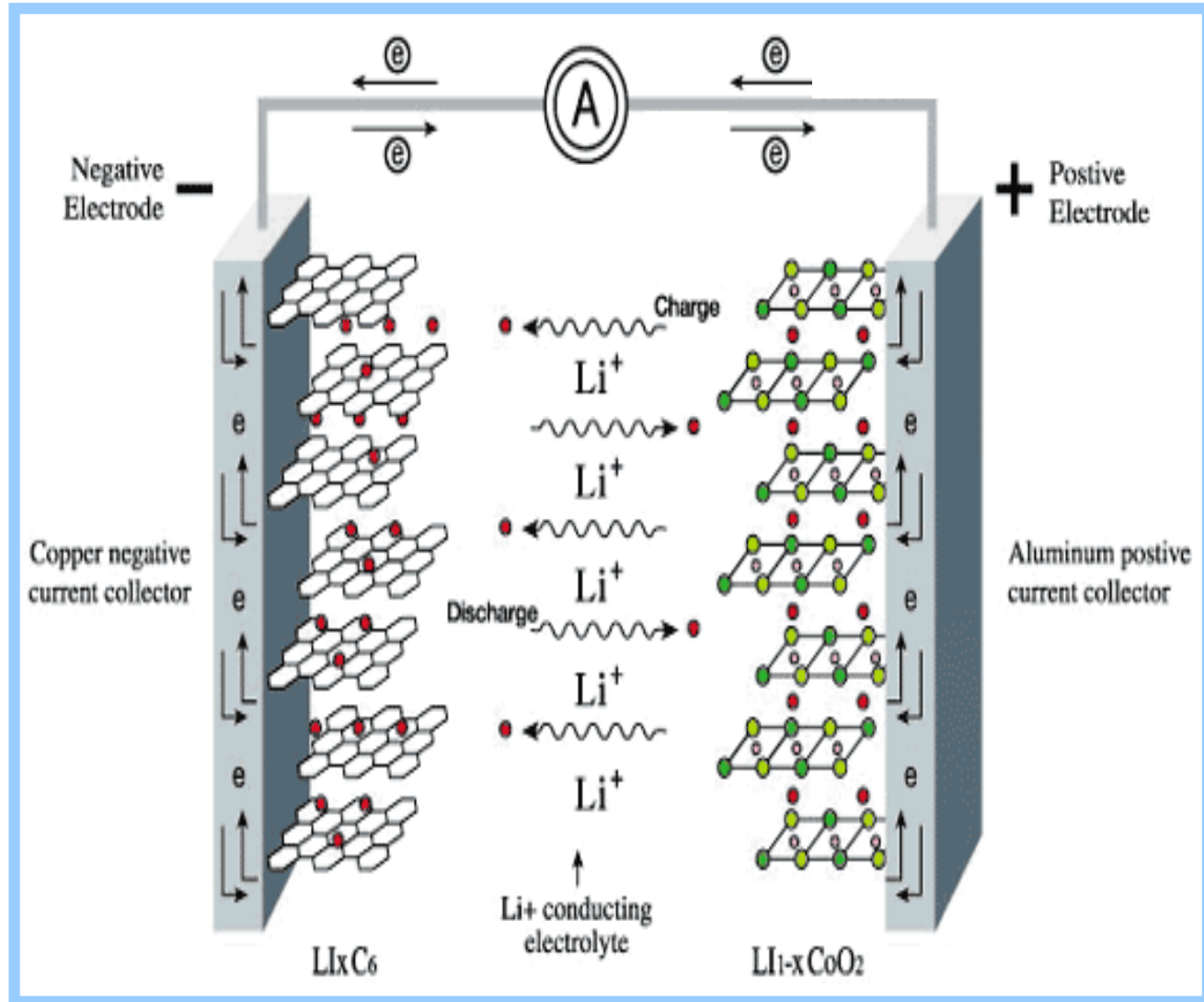


Figure 7.3 Insertion of lithium (solid black circles) into the gallery space of titanium disulfide.

Lithium rechargeable battery



Nobel Prize in Chemistry, 2019

Li rechargeable battery



존 굿이너프

John B. Goodenough



스탠리 휘팅햄

M. Stanley Whittingham



아키라 요시노

Akira Yoshino

Insertion reaction electrodes

- 1976 **Whittingham**, $x\text{Li} + \text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2$, $x: 0\sim 1$
 - insertion-driven solid solution redox process
 - reversible over many cycles

M. S. Whittingham,
Science 192, 1126
(1976).

M. S. Whittingham,
J. Electrochem. Soc.
123, 315 (1976).

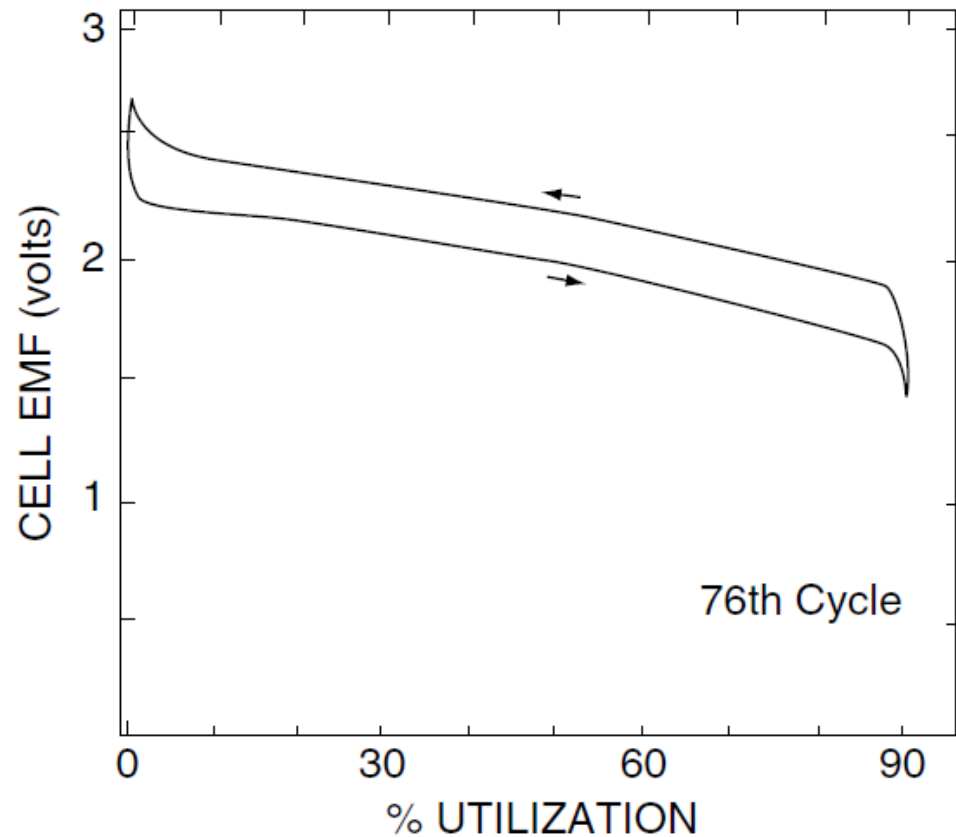


Fig. 9.1 Charge/discharge behavior of a Li/TiS₂ cell after 76 cycles

R. A. Huggins, *Advanced Batteries*, Springer, 2009.

Goodenough

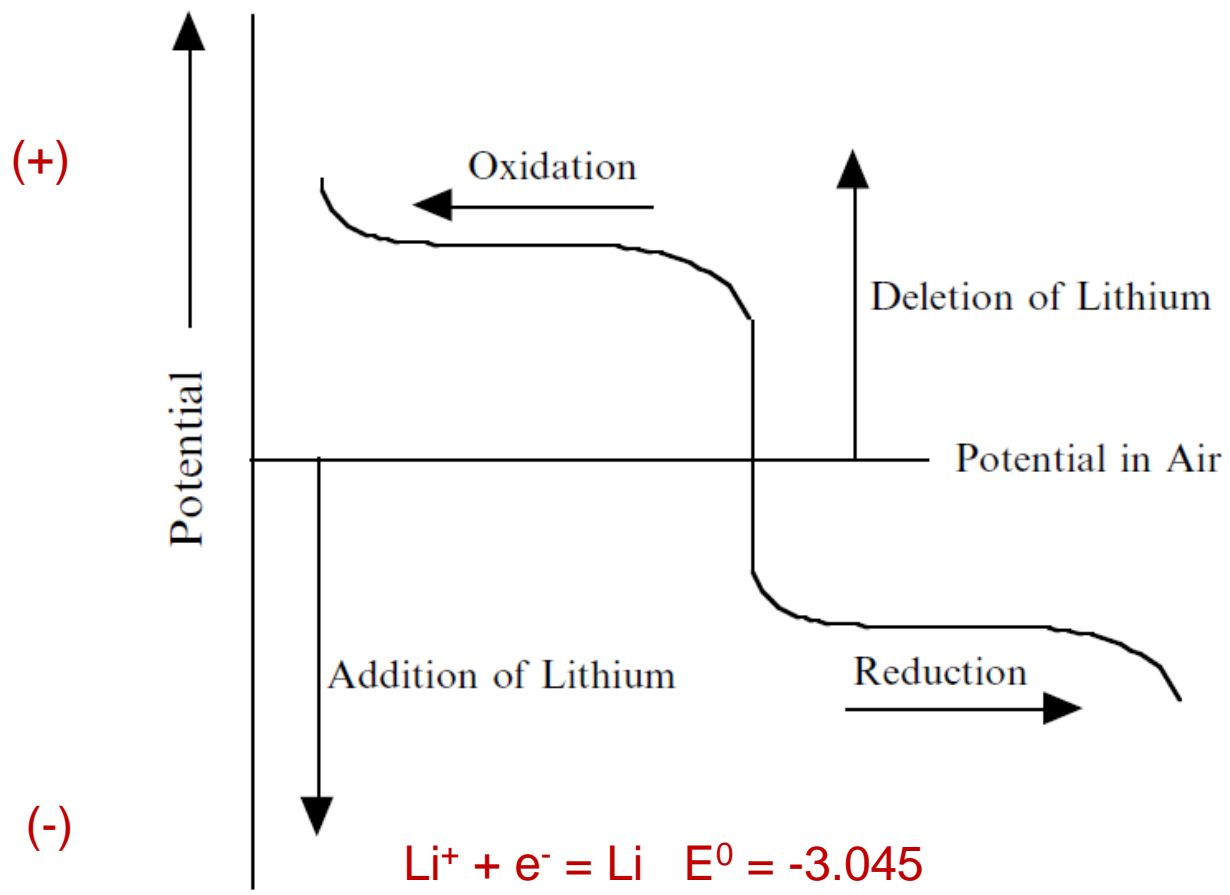


Fig. 9.3 Schematic of the behavior of a material that is amphoteric, i.e., that can be both electrochemically oxidized at high potentials by the deletion of lithium, and electrochemically reduced at lower potentials by the addition of lithium

-This approach, involving the use of materials in which lithium is already present, was first demonstrated in Prof. **Goodenough**'s laboratory in Oxford. The first examples of materials initially containing lithium, and electrochemically deleting lithium from them, were the work on $\text{Li}_{1-x}\text{CoO}_2$ [12] and $\text{Li}_{1-x}\text{NiO}_2$ [13] in 1980. They showed that it is possible in this way to obtain high reaction potentials, up to over 4V.

[12] K. Mizushima, P.C. Jones, P.J. Wiseman and J.B. Goodenough, Mater. Res. Bull. 15, 783 (1980).

[13] J.B. Goodenough, K. Mizushima and T. Takada, Jpn. J. Appl. Phys. 19 (Suppl. 19-3), 305 (1980).

→ SONY of a lithium battery containing a carbon negative electrode and a LiCoO_2 positive electrode that became commercially available in 1990

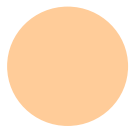
→ assembled in the discharged state. They were activated by charging, whereby lithium left the positive electrode material, raising its potential, and moved to the carbon negative electrode, whose potential was concurrently reduced.

This cell can be represented as



and the cell reaction can be written as





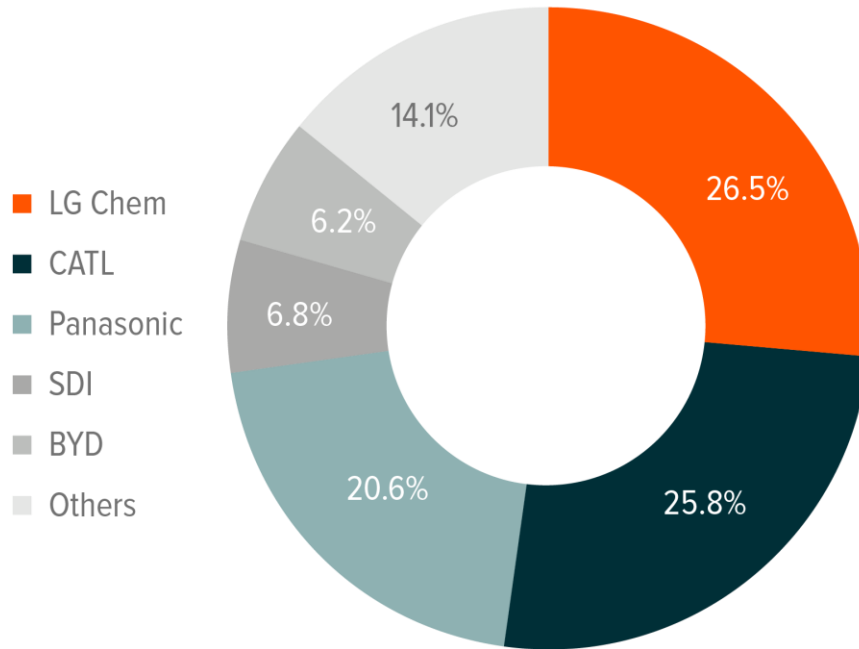
History of secondary battery



Date	Type	Chemistry
1860	Lead-acid 납축전지	$PbO_2/H_2SO_4/Pb$
1900	Edison cell	$Ni/2NiOOH/Fe$
	Ni-Cd cell	$Ni/2NiOOH/Cd$
1965	Beta cell	$Na/\beta-Al_2O_3/S$
1970	Zinc-chlorine	$Zn/ZnCl_2/Cl_2$
1980-90	Li/SSE	$Li/PC-Li_2ClO_4/MX_2$
	Polymeric cells	$Li/PEO-LiClO_4/TiS_2$
	Glassy cells	$Li/Li^+-glass/TiS_2$
1991	Li microbatteries	$Li/Li^+-glass/TiS_2$
1992	Rocking-chair cells	$LiMn_2O_4/elect./carbon$
	리튬이차전지	$LiCoO_2/elect./carbon$
		$LiNiO_2/elect./carbon$

EV BATTERY MARKET SHARE (CUMULATIVE JAN-AUG 2020)

Source: Global X ETFs, The Korea Herald. Note: Cumulative battery capacity from January to August 2020.



COMPANY	GIGAWATT-HOURS (GWH)
LG Chem	15.9
CATL	15.5
Panasonic	12.4
SDI	4.1
BYD	3.7
SKI	2.7
AESC	2.2
Guoxuan	1.2
PEVE	1.2
CALB	1.2

 **LG Energy Solution**
ESS Battery Division

 **LG Chem**

SAMSUNG SDI

 **SAMSUNG**

 **SK innovation**

 **HYUNDAI**

Table 7.2 Common Negative Electrode Materials for Batteries. Values Are Theoretical

Element	MW [g·mol ⁻¹]	Standard potential [V]	Density [g·cm ⁻³]	Valence	Specific capacity [A·h·g ⁻¹]	Volumetric capacity [A·h·cm ⁻³]
Li	6.941	-3.01	0.534	1	3.86	2.06
Na	22.99	-2.714	0.971	1	1.16	1.12
Mg	24.305	-2.4	1.738	2	2.20	3.8
Al	26.98	-1.7	2.699	3	2.98	8.1
Fe	55.845	-0.44	7.86	2	0.96	7.5
Zn	65.39	-0.763	7.13	2	0.82	5.8
Cd	112.41	-0.403	8.65	2	0.48	4.1
Pb	207.21	-0.126	11.34	2	0.26	2.9

Theoretical capacity and state of charge

-The capacity is a rating of the charge or energy stored in the cell
→ [A·h] or [W·h], $W·h = A·h \times V_{ave}$, $A = C/s \rightarrow 1 Ah = 3600 C$

$$\text{Theoretical capacity of electrode} = m_i n F / M_i \text{ [C]}$$

m_i : the mass of active material, M_i : its molecular weight
→ theoretical capacity expressed in units as Ah/kg, Ah/g, mAh/g
→ the theoretical capacity for electrode and cell (two electrodes)

Illustration 7.1

-State of charge (SOC) or state of discharge (SOD, or depth of discharge (DOD)) to quantify the available capacity remaining in a cell while in use

Fig. 7.4

When the cell is fully charged or at 100% SOC, pure Zn and Ag_2O are present. As the reaction proceeds the reactants to ZnO and Ag

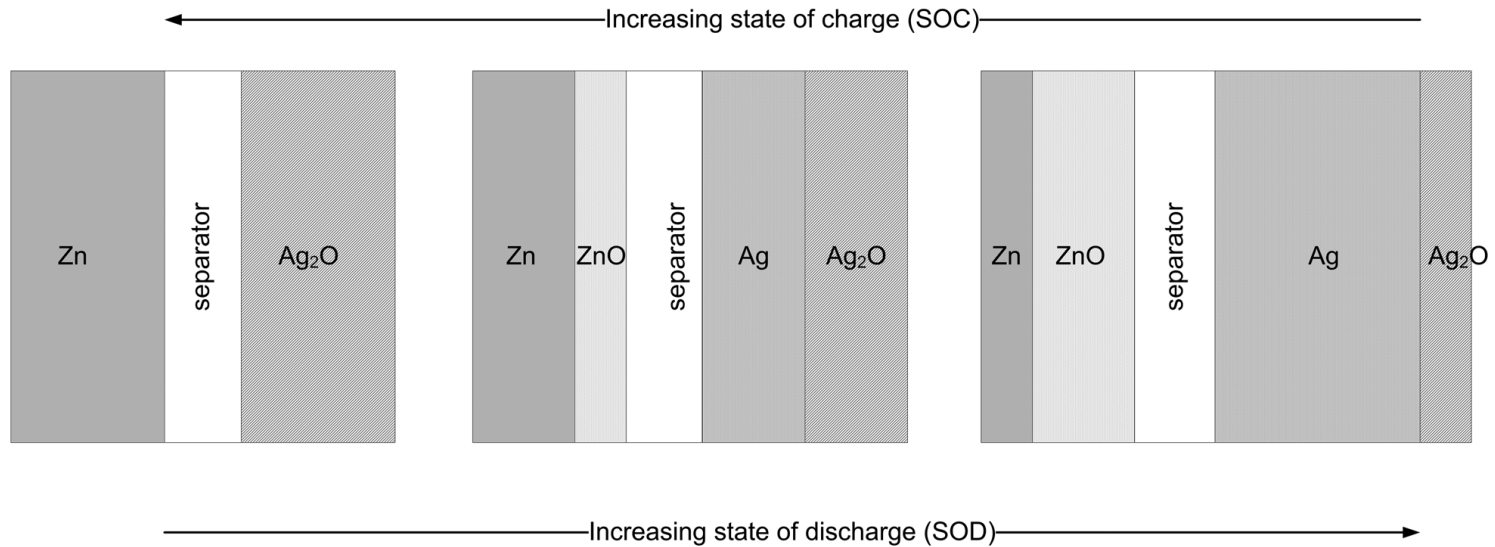


Figure 7.4 State of charge as conversion of active material.

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 Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

$$\text{SOC} = \text{available capacity remaining} / \text{total capacity} \times 100\%$$

$$\text{SOD} = 100 - \text{SOC}$$

An electric vehicle (battery) Specification

e.g. 300 km driving distance

40 kWh battery, Power 90 kW

(Energy density 140 Wh/kg, Power density 250 W/kg)

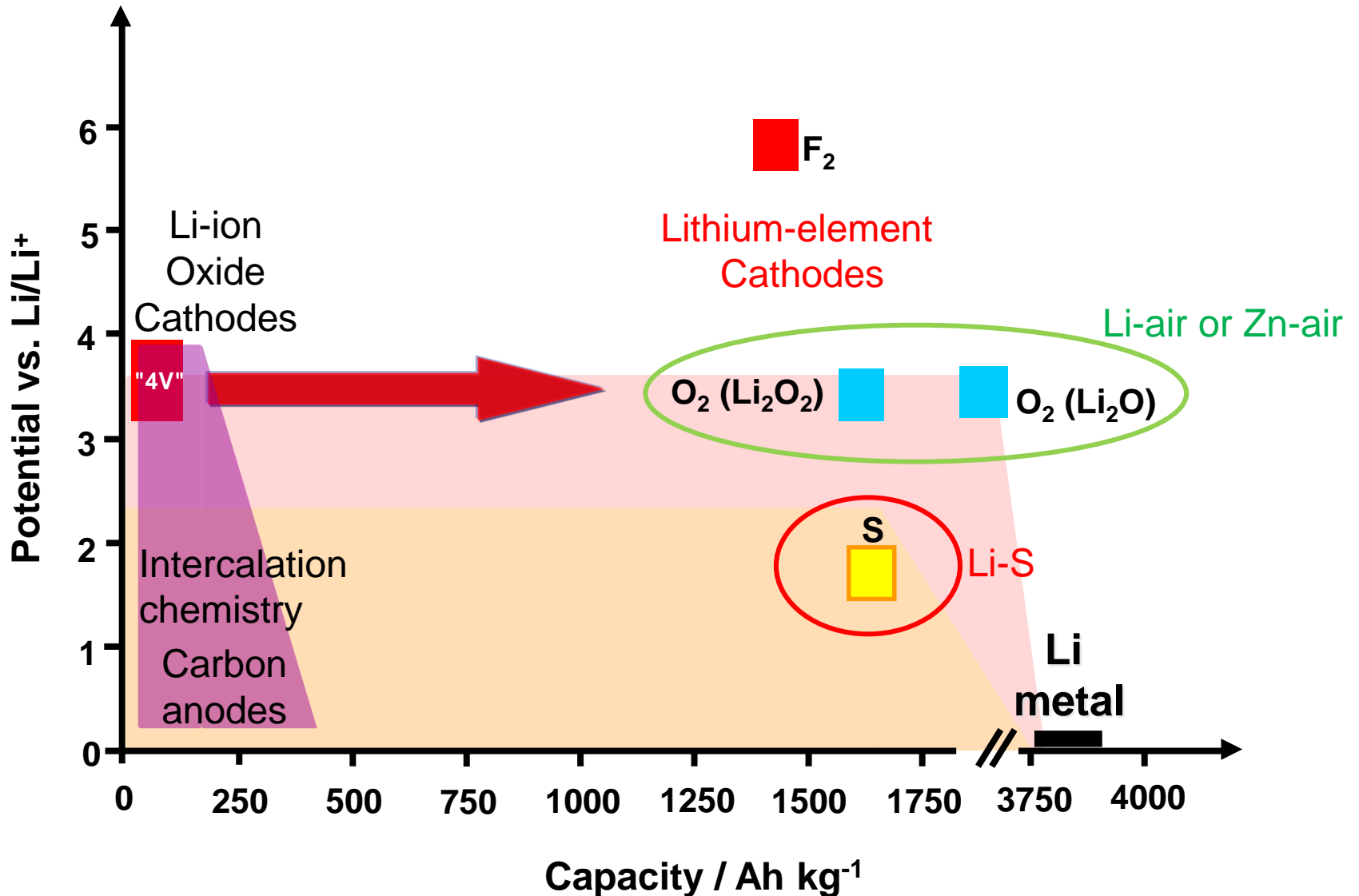
550 Wh/L

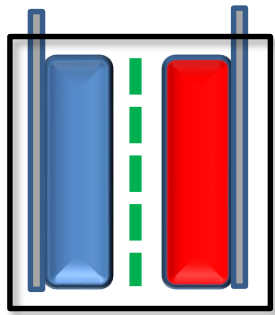
Battery weight 300 kg

Efficiency 7 km/kWh

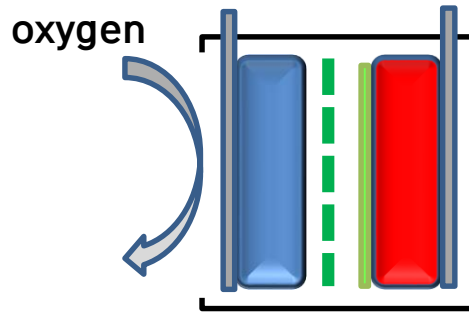
cf. Gasoline engine: ~800 km, 60~70 *liter* tank, 12 km/*liter*

Advanced batteries

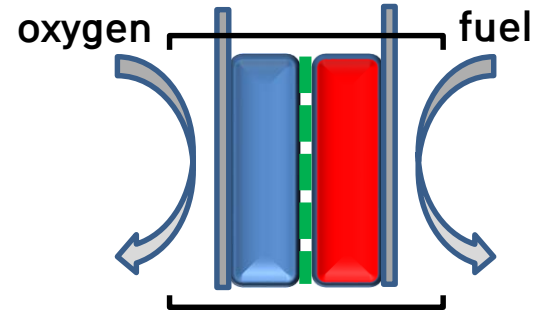




Li-S Battery

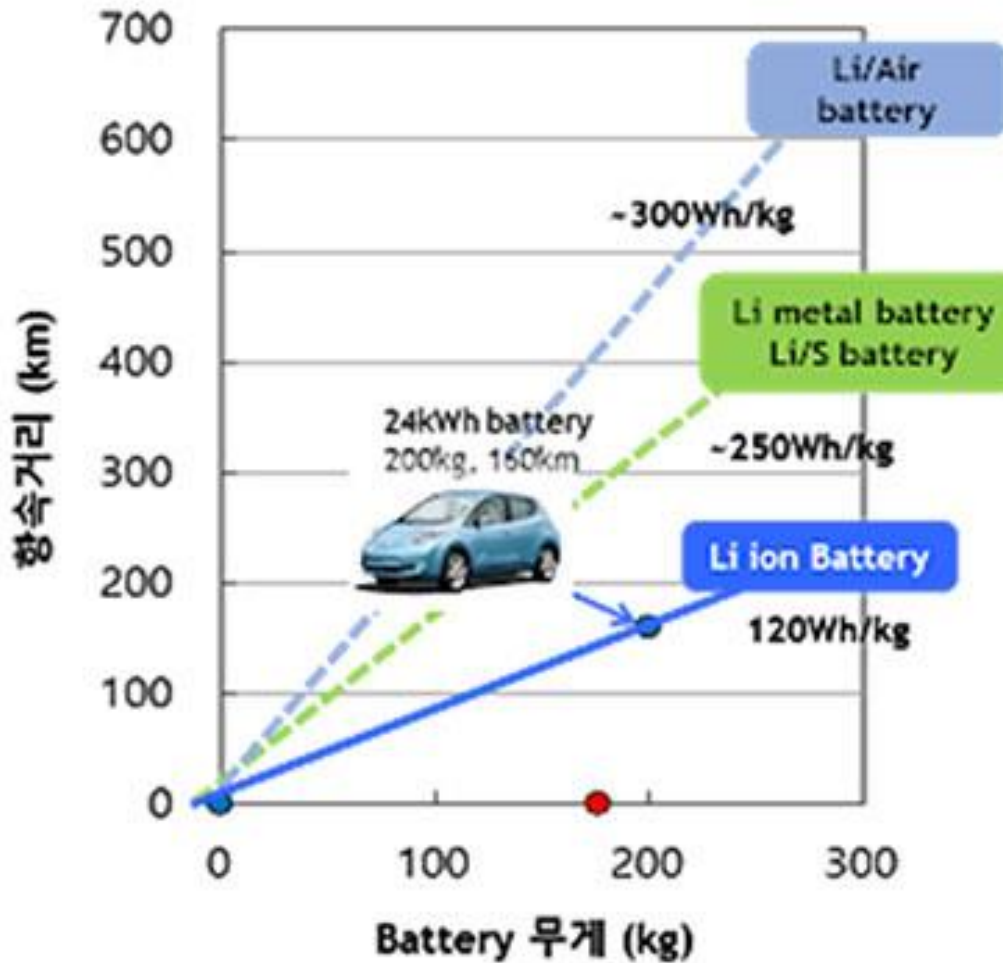


Li-Air Battery

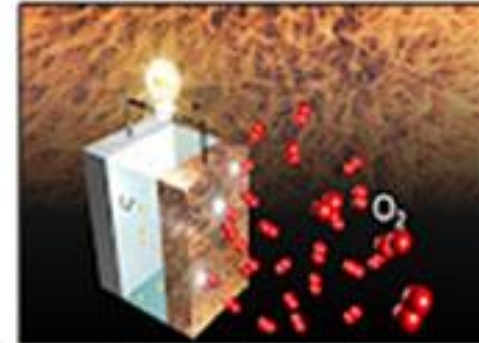


Fuel Cell

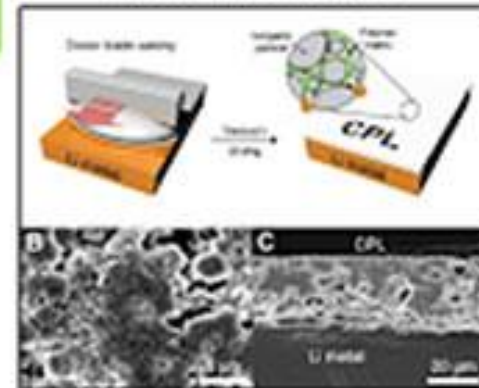
Flow Battery
All Solid Battery



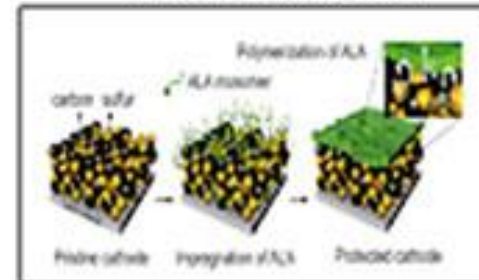
Metal/Air Batteries



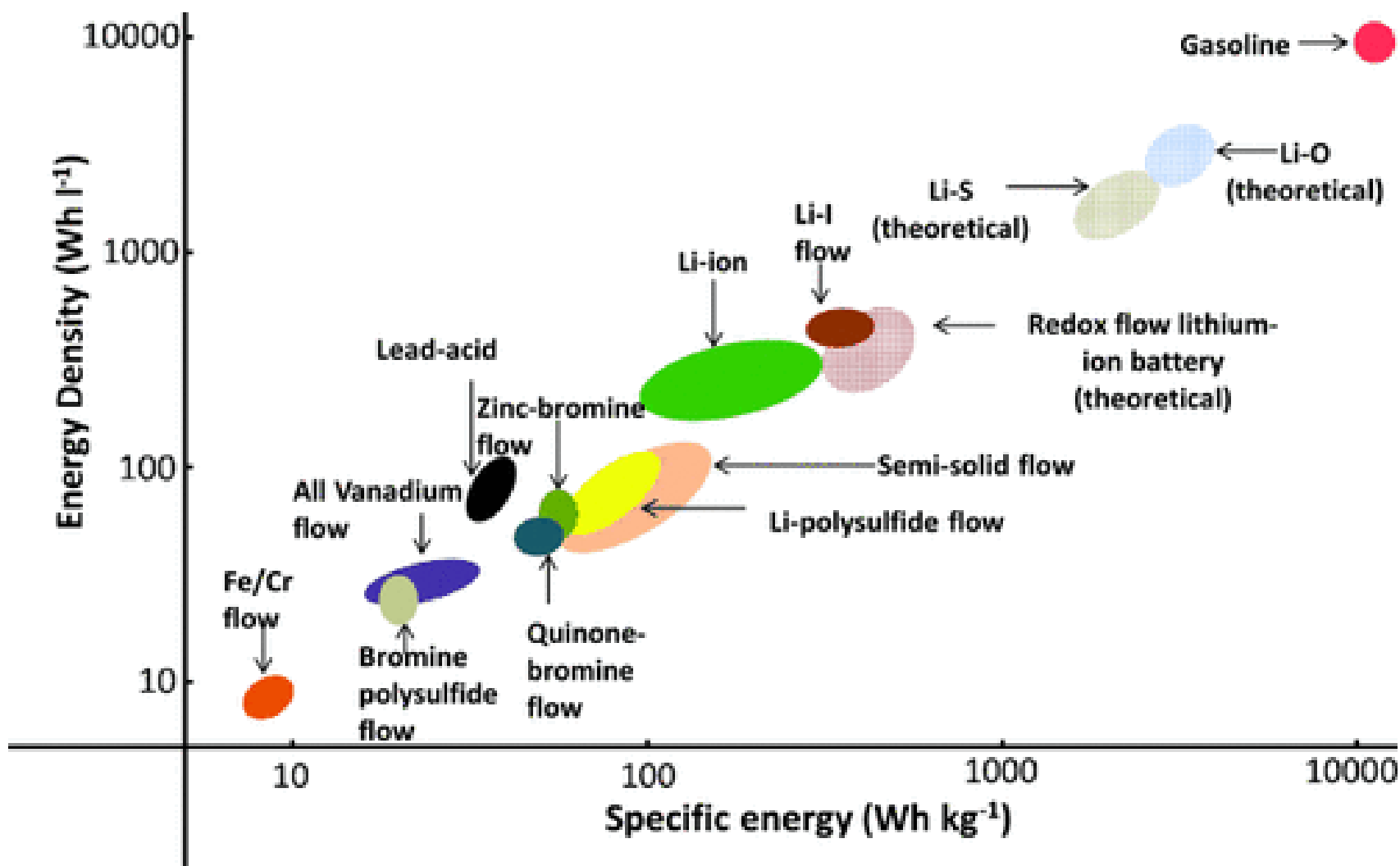
Li Metal Batteries



Li Sulfur Batteries



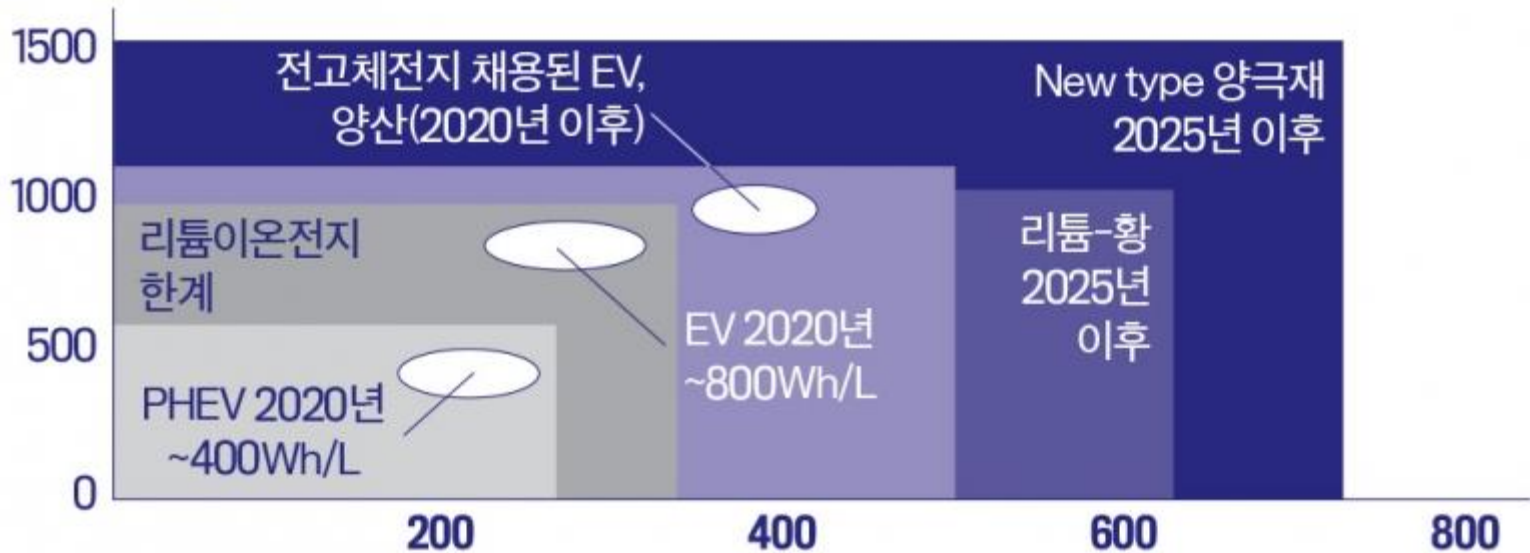
From Prof. Hee-Tak Kim's homepage (KAIST)



전기차용 이차전지 기술전망

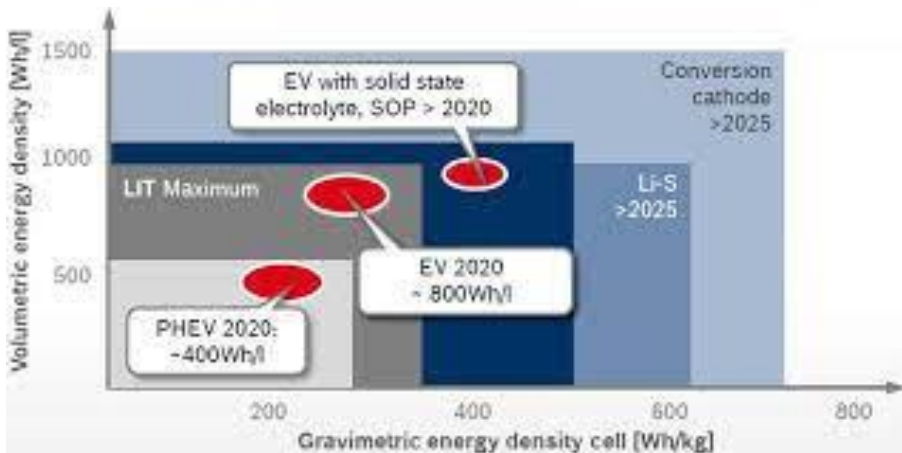
리튬이온전지 차세대 전지

부피 에너지 밀도(Wh/L)



무게 에너지 밀도(Wh/Kg)

자료: 중소벤처기업부

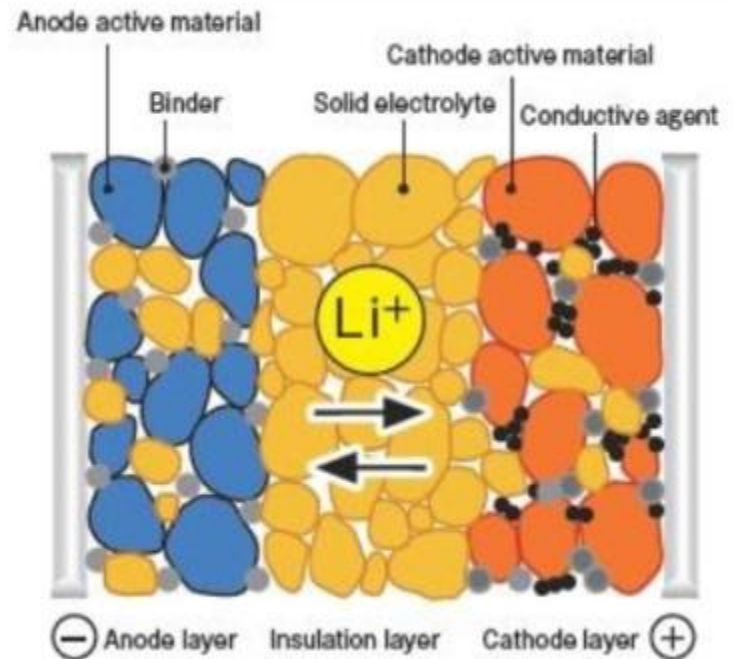
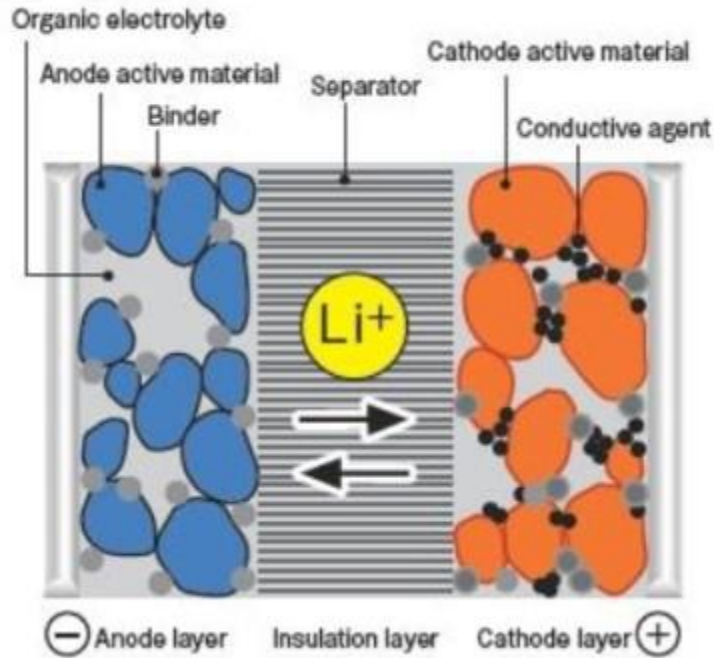


Li-ion Battery

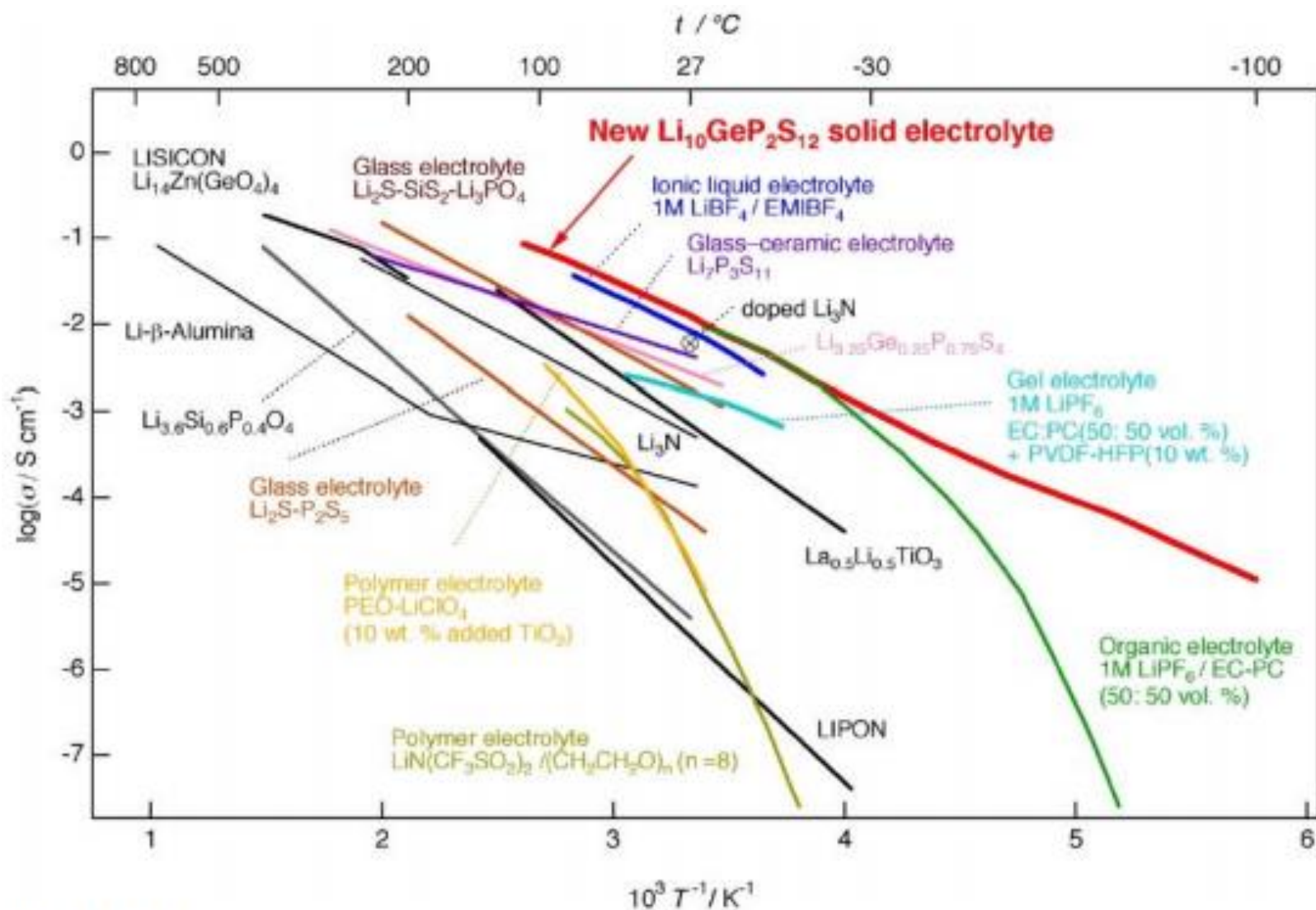
All Solid State Battery

전통 리튬이온전지

전고체 리튬이온전지



All Solid State Battery



자료: 전자부품연구원

KETI

Cell characteristics & electrochemical performance

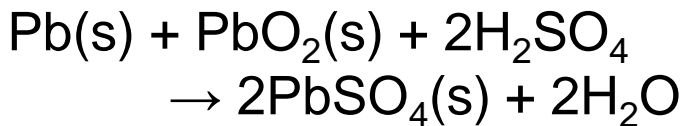
(1) Potential as a function of capacity (SOD)

-In general, the cell potential decreases with increasing SOD (decreasing SOC) → depending on the cell chemistry, the slope of the curves can vary

NiCd battery: flat between 20 and 80% SOD

Lead-acid battery: decreases steadily over the entire range

Discharge:



$$E = E^0 + (RT/F)\ln(a_{\text{H}_2\text{SO}_4}/a_{\text{H}_2\text{O}})$$

Solid component → unit(1)

As discharged, $E \downarrow$ (sloping) related to the dilution of electrolyte during discharge

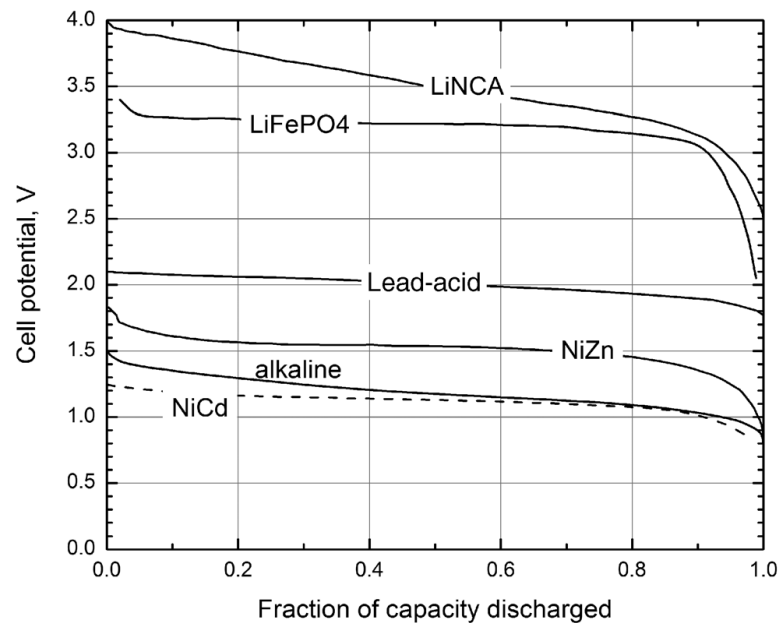
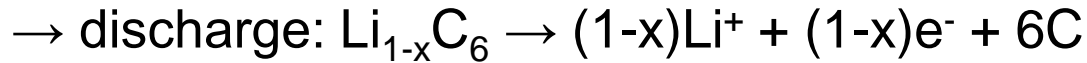


Figure 7.5 Potentials of several battery chemistries.

-Insertion reactions

(i) Negative electrode: Li in carbon in lithium-ion battery



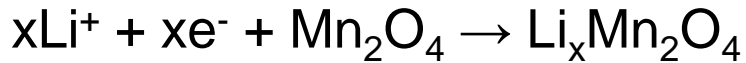
→ only a few % volume change with insertion of lithium

→ potential varies with the amount of lithium inserted (solid solution)

(ii) Positive electrode:

LiMn_2O_4 (spinel structure)

→ discharge:



$x = 0$ (fully charged)

$x \uparrow$ as discharged

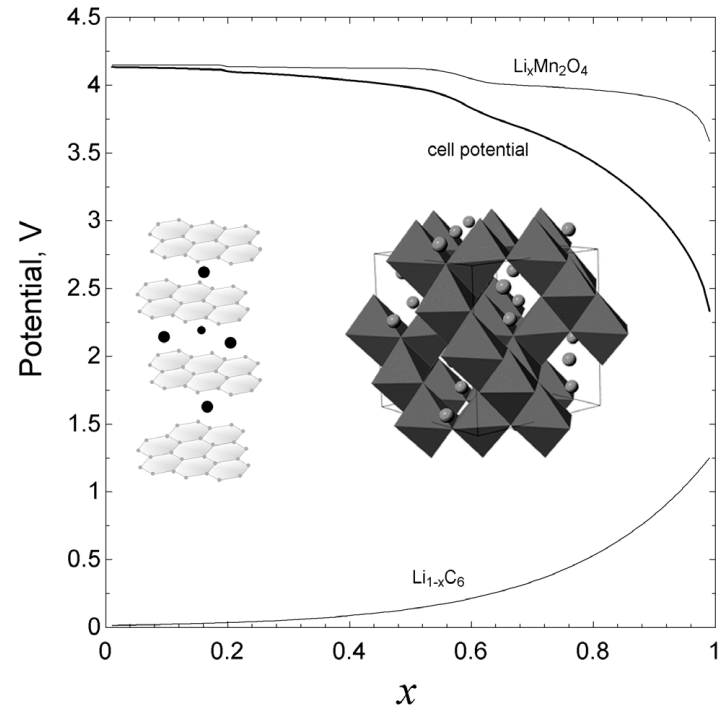


Figure 7.6 Potential versus the fraction discharged for a lithium-ion cell. Also shown are the structural aspects of the negative electrode (a) and positive electrode (b).

cf. Shape of discharge curves and the Gibbs phase rule

-discharge curves: flat or S-shape(slope)

→ **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)



(-)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

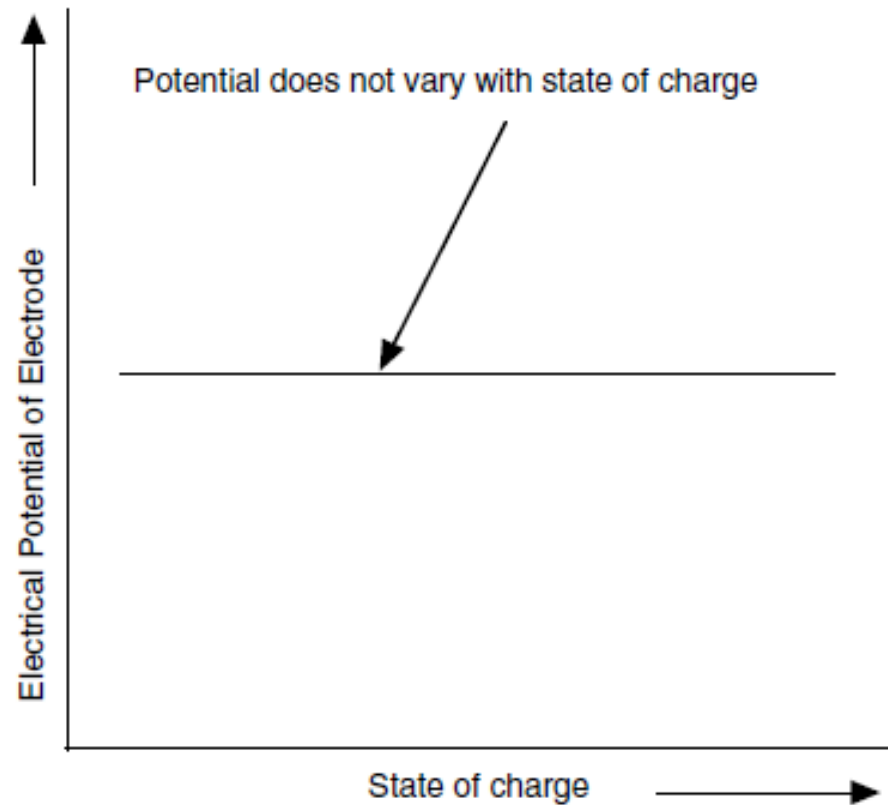


Fig. 2.4 Potential of a pure lithium electrode does not vary with the state of charge of the LiI cell

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

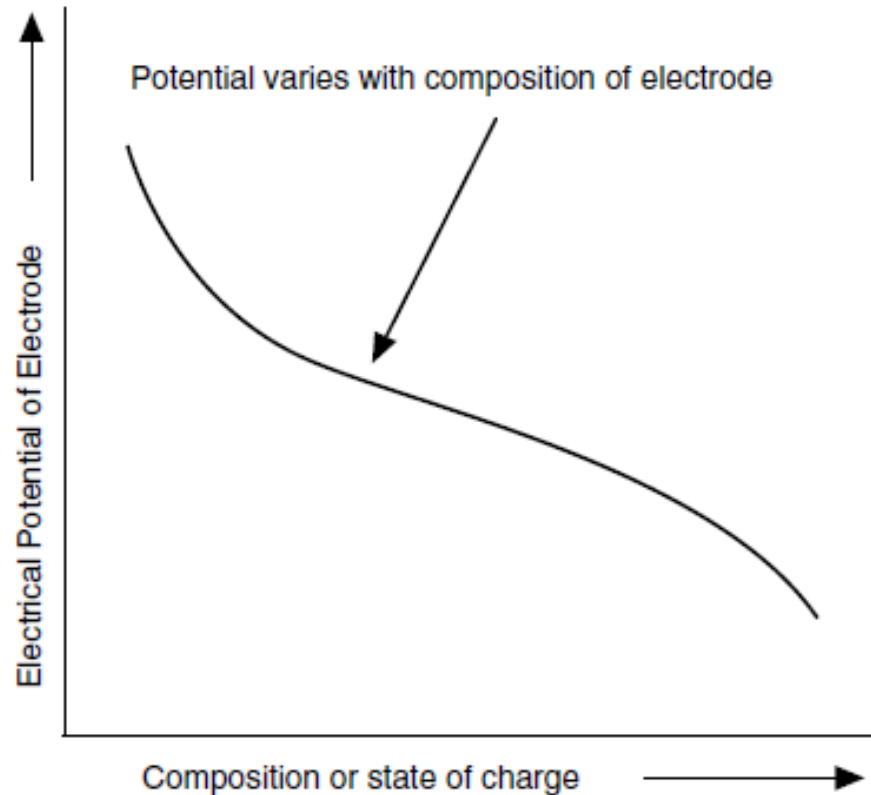


Fig. 2.5 Schematic representation of the variation of the electrical potential of an electrode as a function of its composition for the case in which the residual value of F is not zero

-Gibbs Phase Rule:

Single-phase regions in a binary system: $F = C - P + 2 = 2 - 1 + 2 = 3 \rightarrow$ electrical potential varies with composition within single-phase regions (at const T & P)

It is composition-independent when two phases are present in a binary system ($F = 2 - 2 + 2 = 2$)

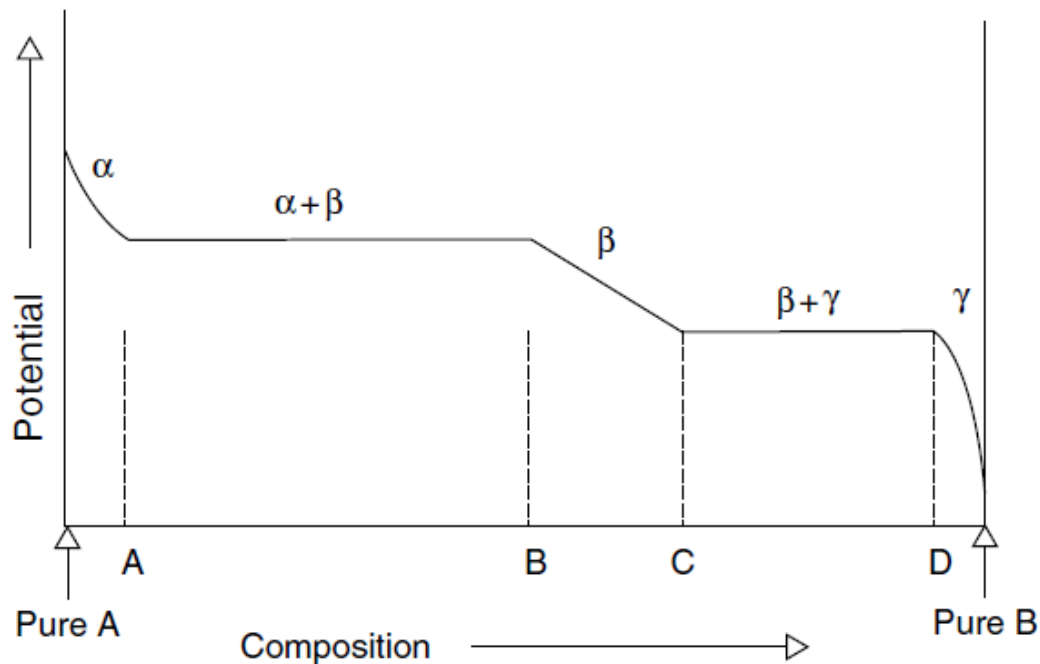


Fig. 3.6 Schematic variation of electrical potential with composition across the binary phase diagram shown in Fig. 3.5

(2) Effect of rate on potential as a function of capacity

-“C-rate”: normalized rate of charge or discharge

→ “1C” rate: the current at which it requires one hour to utilize the capacity of the battery

e.g. 5 Ah battery: 5 A for 1h →
5 A corresponds to the 1 C-rate.

0.5 A for 10h: C/10

Fig. 7.7

During discharge, potential of the cell is always less than the equilibrium or thermodynamic potential

$$E^0 - V_{\text{cell}} = \eta$$
$$= |\eta_{\text{ohmic}}| + |\eta_{\text{neg}}| + |\eta_{\text{pos}}| + |\eta_{\text{conc}}|$$

During discharge, potential of the cell ↓
with current ↑ due to polarization
(during charge, potential of the cell is
greater than equilibrium potential)

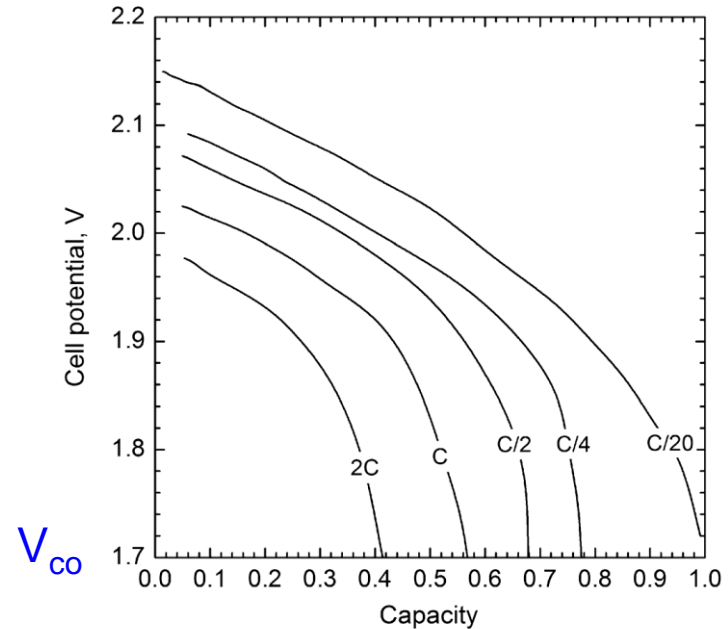


Figure 7.7 Effect of rate on potential as a function of the fractional capacity for a lead–acid cell.

The Rate of Charging or Discharging as Expressed in Terms of the “C-Rate”

C- rate, h ⁻¹	Discharge time, hours
C/20	20 hours
C/5	5 hours
C	1 hour
2C	30 minutes
10C	6 minutes

- Equilibrium potential (E^0 or U):** potential of cell described by thermodynamics. The potential depends on the materials, temperature, pressure, and composition
- Open-circuit voltage (V_{ocv}):** Potential of the cell when no current is flowing, not necessarily equal to the equilibrium potential
- Nominal potential:** typical potential of the cell during operation, this will be less than the thermodynamic potential when discharging
- Average voltage:** potential averaged over either the discharge or charge
- End or cutoff voltage (V_{co}):** potential of the cell when the discharge is terminated

-Ohmic polarization →
largest contribution to the cell polarization

Illustration 7.2

-Resistance can change during discharge

Lead-acid battery:

$H_2SO_4 \downarrow$ during discharge → resistance \uparrow

Ni-Cd battery: hydroxyl ion not consumed

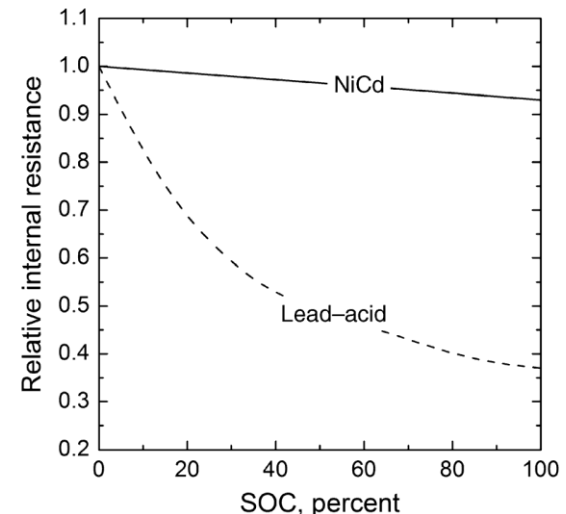


Figure 7.8 Change in cell resistance with state of charge. A fully discharged cell has a value of unity.

-Activation or kinetic polarization → kinetic losses typically do not vary linearly with the current, most significant at low currents

-Semiempirical Shepherd equation

Illustration 7.3

-Capacity vs. temperature

→ temperature ↑ →

ohmic/concentration/kinetic polarization ↓

Temperature is enemy of long battery life

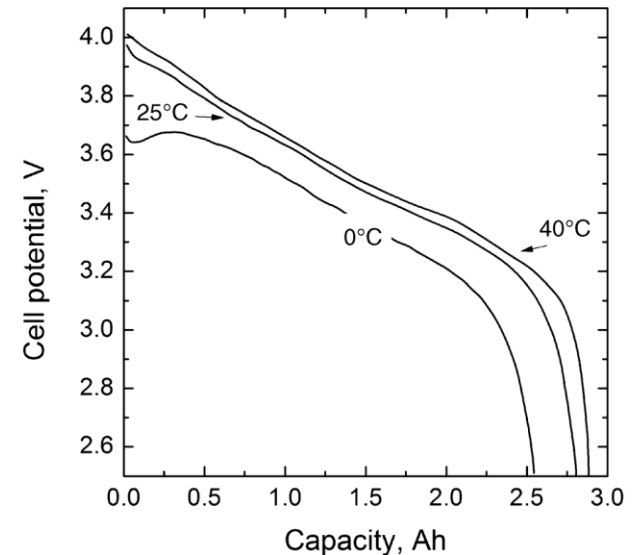


Figure 7.9 Effect of temperature on the cell voltage during discharge for a lithium-ion cell.

Ragone plots

-Power and energy are key design aims of an electrochemical system for energy storage and conversion

Power [W, kW], $P_{ave} = (1/t_d) \int IV(t)dt$

specific power [kW/kg],
specific energy [kWh/kg],
power density [kW/L],
energy density [kWh/L]

-Ragone plot:
trade-off between power and energy

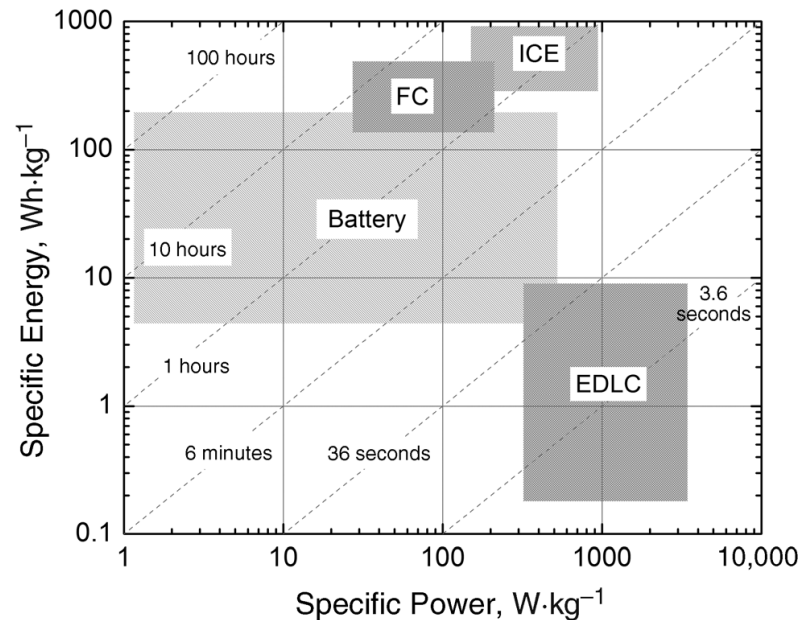


Figure 7.10 Ragone plot illustrating the strengths of different energy storage and conversion devices.

Heat generation

- heat generation in battery plays an important role in cell performance, system design, battery safety, cell life
- Heat can be generated in electrochemical cells due to irreversible losses associated with kinetics and concentration overpotentials, by resistive or Joule heating associated with the flow of current in solution, and by reversible changes due to differences in the entropy of reactants and products

Heat generation,
 $q = I(E^0 - V_{\text{cell}}) - I[T(\partial U/\partial T)]$ [W]
entropic contribution

Fig. 7.11
Nonlinearly increase
Increase with current

Illustration 7.5
Illustration 7.6

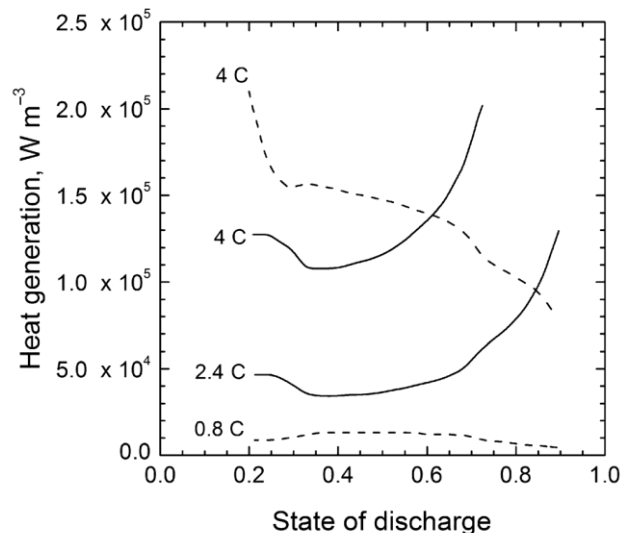


Figure 7.11 Rates of heat generation for a lithium-ion cell. Solid lines are for discharges and dashed lines are for charges. (Adapted from *J. Power Sources*, **247**, 618 (2014).)

Efficiency of secondary cells

-The most basic efficiency of a rechargeable cell is the **coulombic efficiency**: refer to a battery that undergoes a complete charge-discharge cycle

$$\eta_{\text{coul}} = \# \text{ of coulombs on discharge} / \# \text{ of coulombs on charge} \times 100\%$$

Typical coulombic efficiency >95% for many rechargeable battery

-**Voltage efficiency**: any polarization of the cell $\uparrow \rightarrow$ the efficiency \downarrow
current density $\uparrow \rightarrow$ the efficiency \downarrow (due to the increased irreversible losses at the higher current)

$$\eta_V = V_{\text{cell}}^d / V_{\text{cell}}^c \times 100\%$$

The average voltage: by integrating over time, $V_{\text{cell}}^d = (1/t_d) \int V(t) dt$

-Energy efficiency: the product of coulombic efficiency x voltage efficiency

$$\text{Energy efficiency} = \eta_{\text{coul}} \eta_V = \text{energy out} / \text{energy in} \times 100\%$$

~90% for rechargeable batteries

Charge retention and self-discharge

-**Charge retention**: the amount of charge, usually expressed as a percentage of capacity, remaining after a cell is stored for a period of time and not connected to an external circuit

-**Self-discharge**: the mechanism by which the capacity of the cell is reduced

e.g. 10% loss in capacity in 5 years for a lithium primary battery

10% loss in 24 h for some nickel-based battery

30% per month for Ni-MH secondary battery

5% per month for lithium secondary battery (reversible self-discharge)

cf. capacity fade: irreversible self-discharge (next topic)

-self-discharge sources

(i) **Electronic short**

$$I_{\text{self-discharge}} = V_{\text{cell}} / R_{\text{short}}$$

(ii) **Shuttle mechanism**

NiCd, Ni metal-hydride battery → ammonium hydroxide (impurity) can be formed from the breakdown of a polymer separator → self-discharge through chemical shuttle mechanism

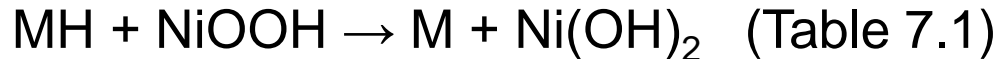
At the positive electrode of the Ni-MH cell,



Transport of nitrite to the negative electrode yields



These two reactions combine to yield



→ these reactions & transport between electrodes result in a chemical short, which discharges the cell

Another shuttle involving the redox reaction of an impurity metal (M)



→ contribute to self-discharge forming chemical short

(iii) Corrosion

Often one or both of the electrodes are thermodynamically unstable in the charged state

e.g. lead-acid battery: grid corrosion & hydrogen evolution → self-discharge reactions

Capacity fade in secondary cells

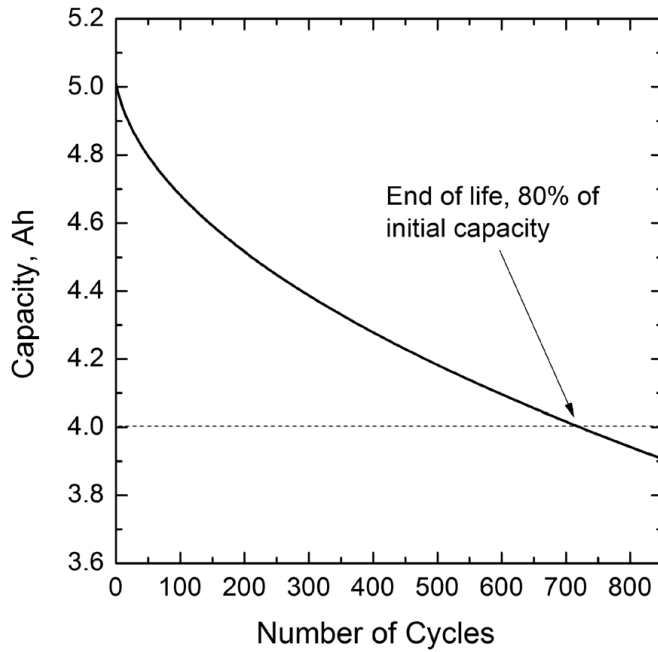


Figure 7.12 Typical behavior for capacity fade of a lithium-ion cell.

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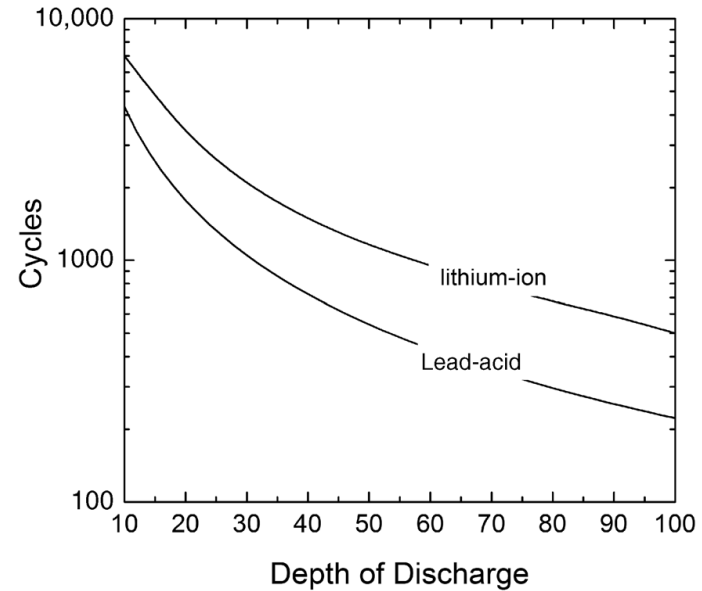


Figure 7.13 Effect of depth of discharge on cycle life.

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