

**Spring Semester, 2011**  
**Energy Engineering**  
에너지공학

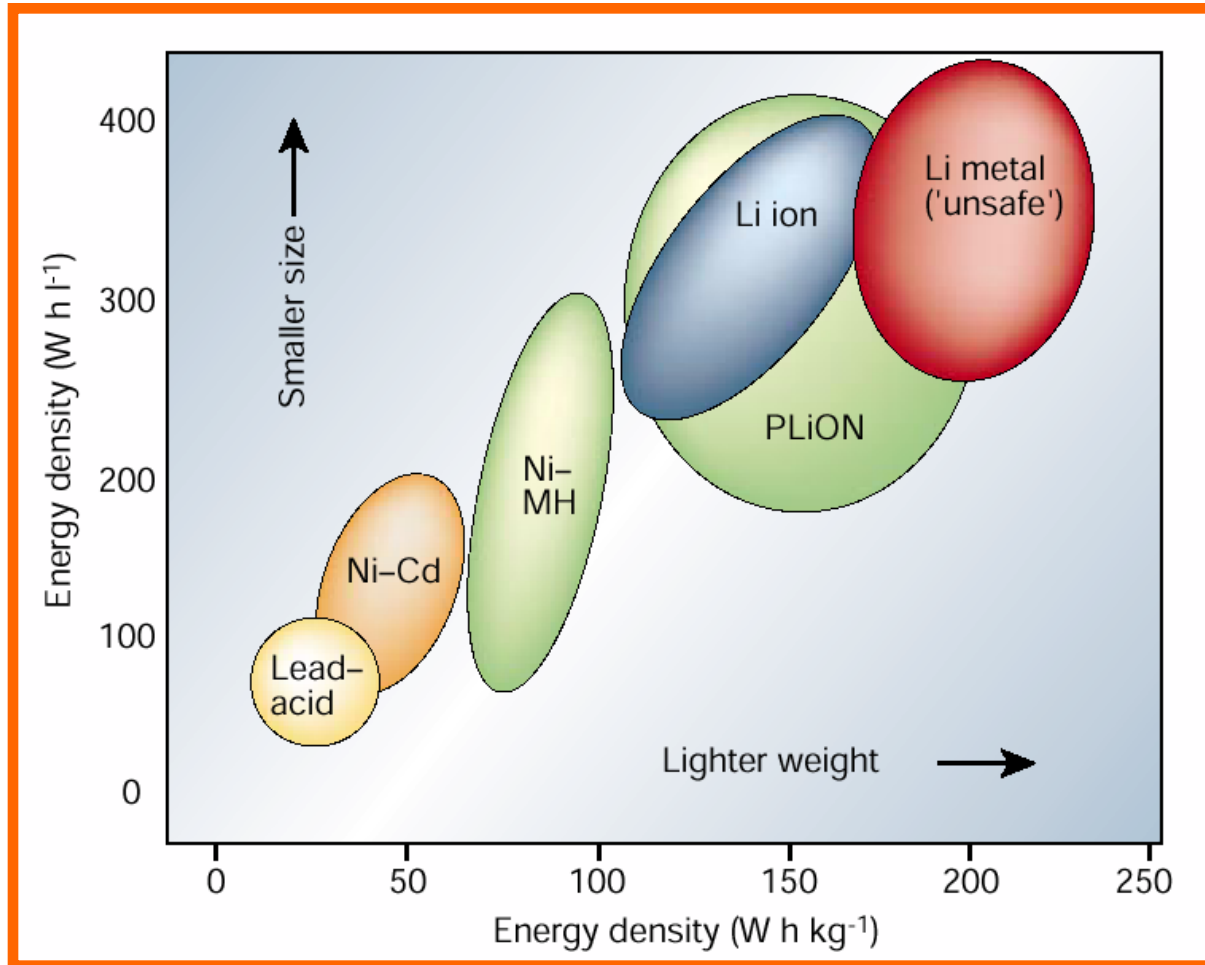
# **Rechargeable Battery**

# History of Secondary Batteries

Date	Type	Chemistry
1860	Lead-acid	$\text{PbO}_2/\text{H}_2\text{SO}_4/\text{Pb}$
1900	Edison cell	$\text{Ni}/2\text{NiOOH}/\text{Fe}$
	Ni-Cd cell	$\text{Ni}/2\text{NiOOH}/\text{Cd}$
1965	Beta cell	$\text{Na}/\beta\text{-Al}_2\text{O}_3/\text{S}$
1970	Zinc-chlorine	$\text{Zn}/\text{ZnCl}_2/\text{Cl}_2$
1980–90	Li/SSE	$\text{Li}/\text{PC-Li}_2\text{ClO}_4/\text{MX}_2$
	Polymeric cells	$\text{Li}/\text{PEO-LiClO}_4/\text{TiS}_2$
	Glassy cells	$\text{Li}/\text{Li}^+\text{-glass}/\text{TiS}_2$
1991	Li microbatteries	$\text{Li}/\text{Li}^+\text{-glass}/\text{TiS}_2$
1992	Rocking-chair cells	$\text{LiMn}_2\text{O}_4/\text{elect.}/\text{carbon}$
		$\text{LiCoO}_2/\text{elect.}/\text{carbon}$
		$\text{LiNiO}_2/\text{elect.}/\text{carbon}$

From Julien, C. and Nazri, G.A., *Solid State Batteries: Materials Design and Optimization*, Kluwer, Boston, 1994. With permission.

# Secondary(or Rechargeable) Batteries

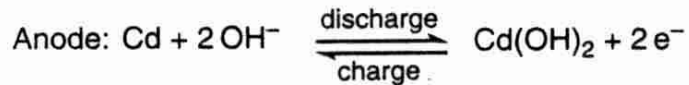
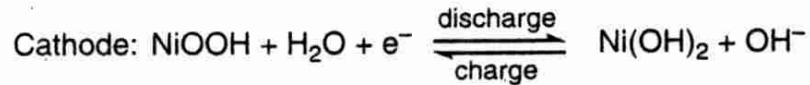


# Comparison of Rechargeable Batteries

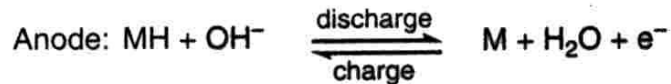
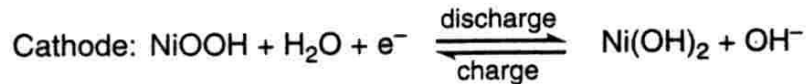
System	Anode	Cathode	electrolyte	Working voltage	Energy density
Lead-acid	Pb	PbO <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub> (aqueous solution)	1.9 V	70
Ni-Cd	Cd	NiOOH	KOH (aqueous solution)	1.2 V	90
Ni-MH	MH	NiOOH	KOH (aqueous solution)	1.2 V	200
Li-ion	C	LiMO <sub>2</sub>	Li-salt	3.6 V	300

# Principles of Rechargeable Batteries

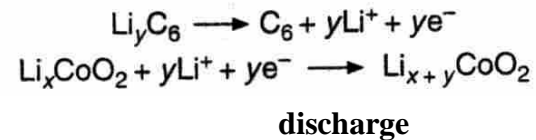
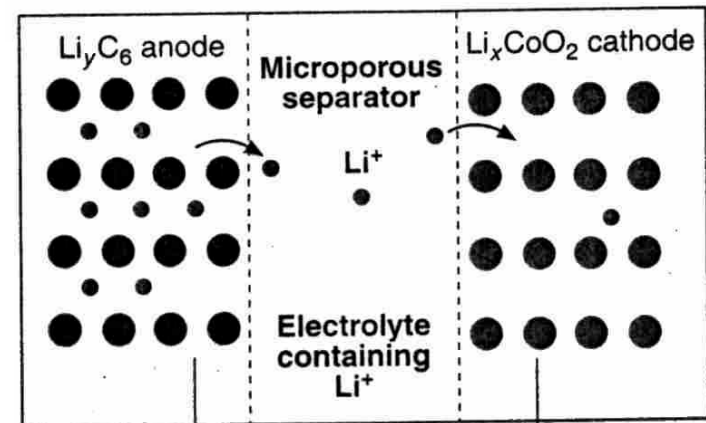
## Nickel-cadmium electrode reactions



## Ni-metal hydride electrode reactions



**Lithium-ion cells discharge by shuttling  $\text{Li}^+$  from anode to cathode through separator**

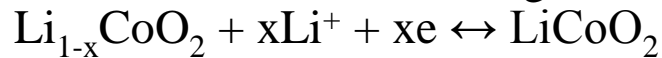


# Electrode Reaction of Li Rechargeable Battery

## Cathode

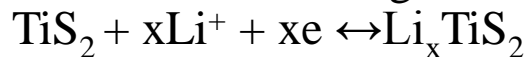
-Oxide (LiMn<sub>2</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, LiCoO<sub>2</sub>, LiNiO<sub>2</sub>)

discharge



-Chalcogenides (MoS<sub>2</sub>, TiS<sub>2</sub> layered structure)

discharge



## Anode

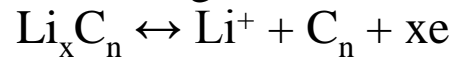
-Lithium (alloy)

discharge

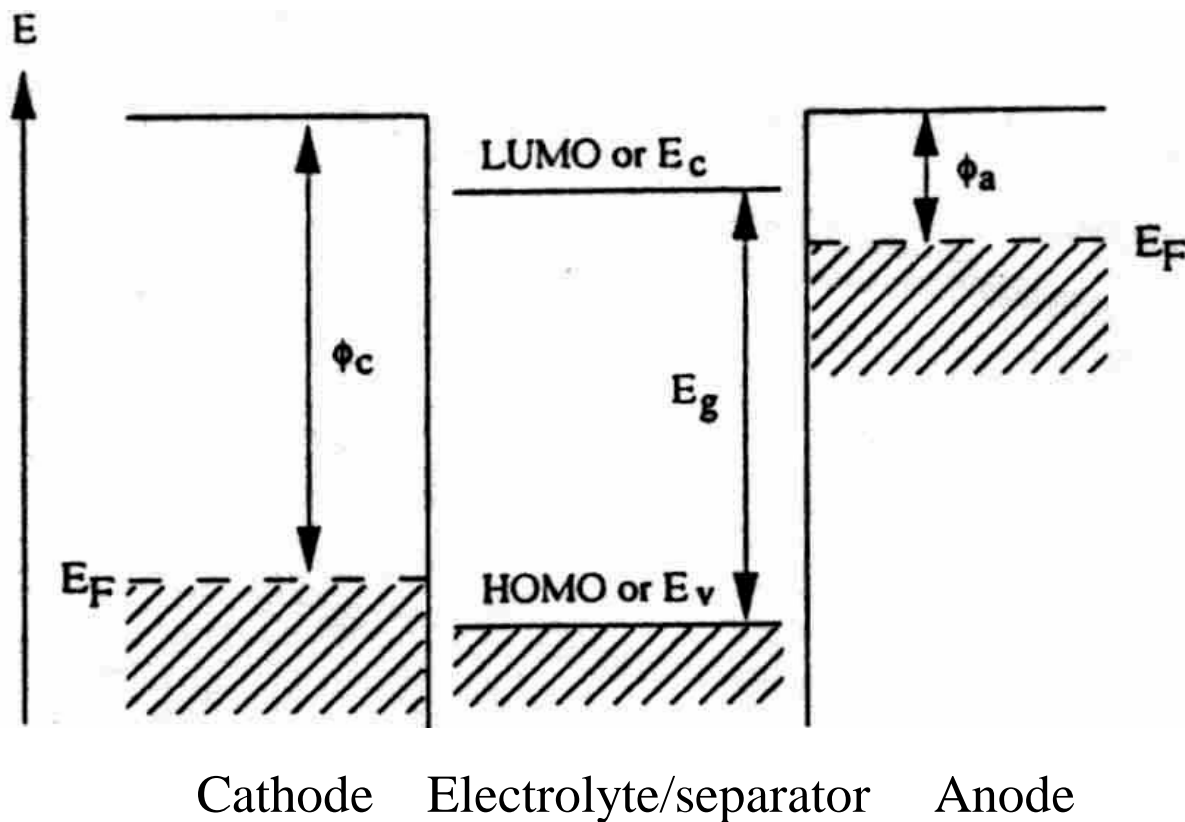


-Carbon compounds

discharge

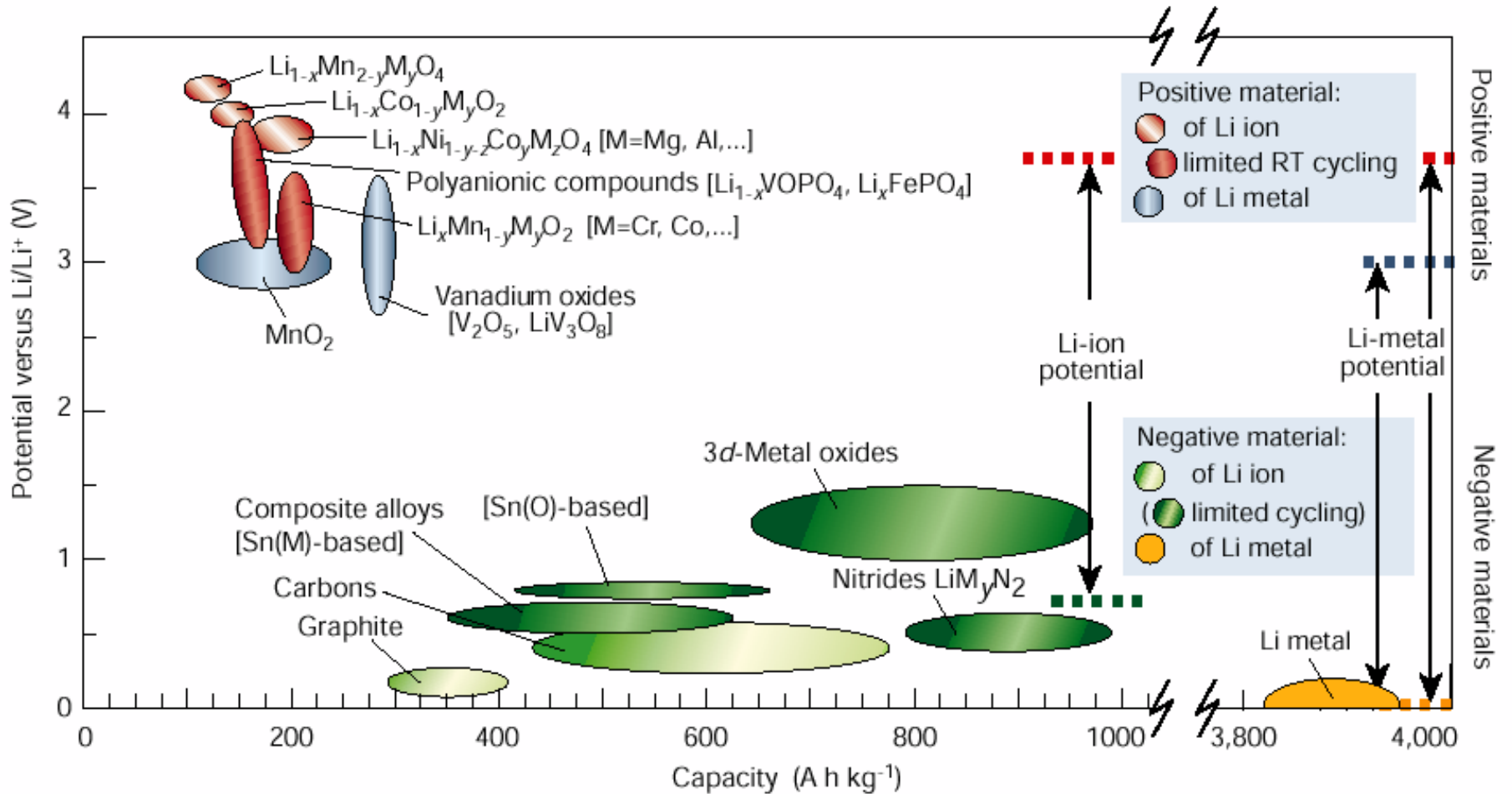


# Energy Diagram of Li Rechargeable Battery



Chemical stability:  
no reduction at  
anode side &  
no oxidation at  
cathode side

# Battery Materials





# Li 이차전지 종류

i) Li metal battery (LMB): Li metal anode

ii) Li ion battery (LIB): carbon anode

iii) Li ion polymer battery (LIPB): carbon anode, liq. Electrolyte + polymer (gel type)

iv) Li polymer battery (LPB): Li metal anode, solid polymer electrolyte

# Energetics of batteries

Three major characteristics of an energy storage device;

- (1) the operating voltage,
- (2) the current that can be drawn at a usable voltage,
- (3) how long it will last

Reaction  $\rightarrow \Delta G^0 = -nFE^0$ , F; 96500 C or 26.8 Ah

## Cell voltage

Actual voltage  $< \Delta G / -nF$ ; overpotential associated with the reaction, resistance losses in the cell, the concentration of the electroactive species in the electrolyte, the way that the cell is discharged  $\rightarrow \Delta G$  gives the maximum possible potential

Voltage starts at the equilibrium value, then falls, eventually reaching zero at some maximum current

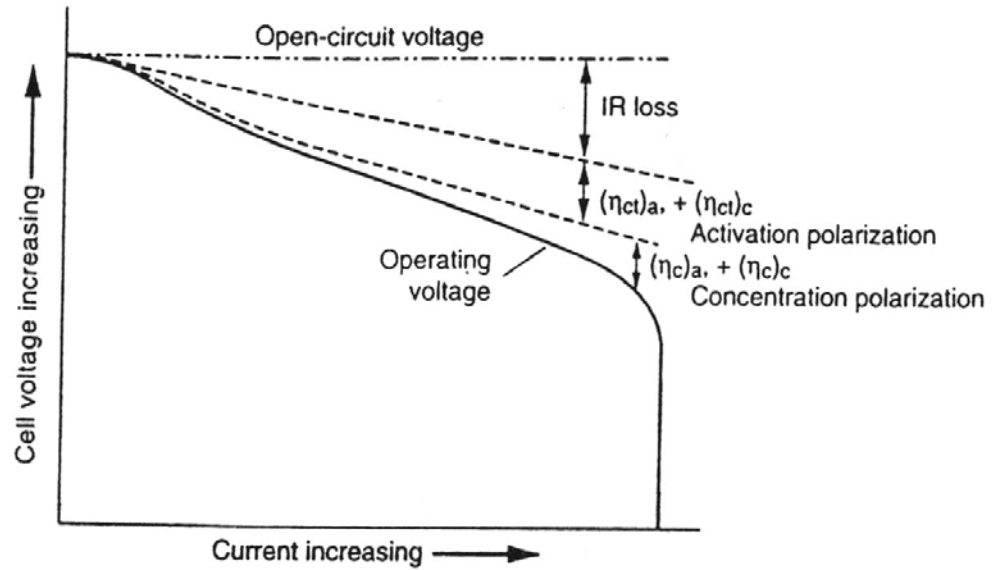
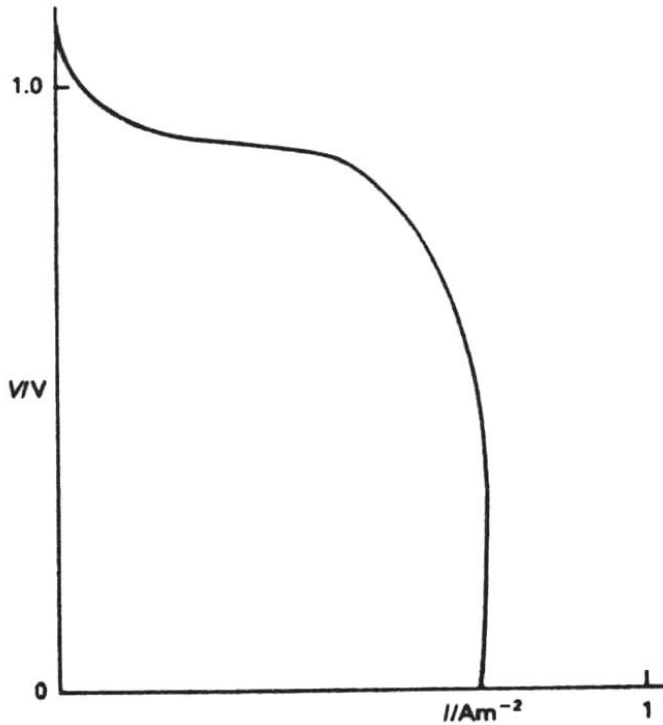


FIGURE 2.1 Cell polarization as a function of operating current.

# Battery Evaluations

**용량** (Capacity , C or Ah)

- the capacity is the amount of charge that may be delivered by a battery
- theoretical capacity

$$C = nF(W/MW)$$

W: weight of active electrode material, MW: molecular weight of material  
F; 96500 C or 26.8 Ah

**전극소재별 이론용량**

1 mol : 96500 C/mol

e.g.

Li: MW 6.941g → 26.8 Ah/6.941 g = 3.861 Ah/g

LiCoO<sub>2</sub>: MW 97.871g → 26.8 Ah/97.871 g = 273.7 mAh/g

**TABLE 1.1** Characteristics of Electrode Materials\*

Material	Atomic or molecular weight, g	Standard reduction potential at 25°C, V	Valence change	Melting point, °C	Density, g/cm <sup>3</sup>	Electrochemical equivalents		
						Ah/g	g/Ah	Ah/cm <sup>3</sup> ‡
<b>Anode materials</b>								
H <sub>2</sub>	2.01	0	2	—	—	26.59	0.037	
Li	6.94	-3.01	1	180	0.54	3.86	0.259	2.06
Na	23.0	-2.71	1	98	0.97	1.16	0.858	1.14
Mg	24.3	-2.38	2	650	1.74	2.20	0.454	3.8
		-2.69†						
Al	26.9	-1.66	3	659	2.69	2.98	0.335	8.1
Ca	40.1	-2.84	2	851	1.54	1.34	0.748	2.06
		-2.35†						
Fe	55.8	-0.44	2	1528	7.85	0.96	1.04	7.5
Zn	65.4	-0.76	2	419	7.14	0.82	1.22	5.8
		-1.25†						
Cd	112.4	-0.40	2	321	8.65	0.48	2.10	4.1
Pb	207.2	-0.13	2	327	11.34	0.26	3.87	2.9
<b>Cathode materials</b>								
O <sub>2</sub>	32.0	1.23	4	—	—	3.35	0.30	
Cl <sub>2</sub>	71.0	1.36	2	—	—	0.756	1.32	
SO <sub>2</sub>	64.0	—	1	—	—	0.419	2.38	
MnO <sub>2</sub>	86.9	1.23‡	1	—	5.0	0.308	3.24	1.54
NiOOH	91.7	0.49†	1	—	7.4	0.292	3.42	2.16
CuCl	99.0	0.14	1	—	3.5	0.270	3.69	0.95
FeS <sub>2</sub>	119.9	—	4	—	—	0.89	1.12	4.35
AgO	123.8	0.57†	2	—	7.4	0.432	2.31	3.20
Br <sub>2</sub>	159.8	1.07	2	—	—	0.385	2.95	
HgO	216.6	0.10†	2	—	11.1	0.247	4.05	2.74
Ag <sub>2</sub> O	231.7	0.35†	2	—	7.1	0.231	4.33	1.64
PbO <sub>2</sub>	239.2	1.69	2	—	9.4	0.224	4.45	2.11

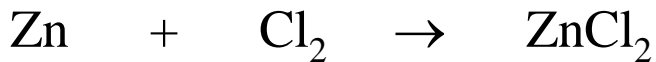
## Energy Density

Battery: portable, electric car → size & weight go together!

## Energy density of Active Materials (Whkg<sup>-1</sup> or Whdm<sup>-3</sup>)

- energy from battery:  $nFE$
- energy density: voltage x storage density (Wh = V x Ah)
- few tens Whkg<sup>-1</sup> of lead-lead acid battery to hundreds for sodium-sulphur

e.g. 1, Zn/Cl<sub>2</sub> cell



0.82 Ah/g    0.76 Ah/g

1.22 g/Ah    1.32g/Ah = 2.54 g/Ah or **0.394 Ah/g**

$$E^0 = 2.12 \text{ V}$$

$$\text{Wh/g capacity} = 2.12 \text{ V} \times 0.395 \text{ Ah/g} = \mathbf{0.838 \text{ Wh/g}}$$

TABLE 1.2 Theoretical Voltage and Capacity of Major Battery Systems\*

Battery	Anode	Cathode	Reaction mechanism	V	Capacity†	
					g/Ah	Ah/kg
Primary						
Leclanché	Zn	MnO <sub>2</sub>	$Zn + 2MnO_2 \rightarrow ZnO \cdot Mn_2O_3$	1.6	4.46	224
Magnesium	Mg	MnO <sub>2</sub>	$Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2$	2.8	3.69	271
Alkaline MnO <sub>2</sub>	Zn	MnO <sub>2</sub>	$Zn + 2MnO_2 \rightarrow ZnO + Mn_2O_3$	1.5	4.46	224
Mercury	Zn	HgO	$Zn + HgO \rightarrow ZnO + Hg$	1.34	5.27	190
Mercad	Cd	HgO	$Cd + HgO + H_2O \rightarrow Cd(OH)_2 + Hg$	0.91	6.15	163
Silver oxide	Zn	Ag <sub>2</sub> O	$Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2Ag$	1.6	5.55	180
Zinc/air	Zn	O <sub>2</sub> (air)	$Zn + \frac{1}{2}O_2 \rightarrow ZnO$	1.65	1.55	658
Li/SO <sub>2</sub>	Li	SO <sub>2</sub>	$2Li + 2SO_2 \rightarrow Li_2S_2O_4$	3.1	2.64	379
Li/MnO <sub>2</sub>	Li	MnO <sub>2</sub>	$Li + Mn^{IV}O_2 \rightarrow Mn^{IV}O_2(Li^+)$	3.5	3.50	286
Reserve						
Cuprous chloride	Mg	CuCl	$Mg + Cu_2Cl_2 \rightarrow MgCl_2 + 2Cu$	1.6	4.14	241
Zinc/silver oxide	Zn	AgO	$Zn + AgO + H_2O \rightarrow Zn(OH)_2 + Ag$	1.81	3.53	283

Secondary						
Lead-acid	Pb	PbO <sub>2</sub>	$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$	2.1	8.32	120
Edison	Fe	Ni oxide	$\text{Fe} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Fe(OH)}_2$	1.4	4.46	224
Nickel-cadmium	Cd	Ni oxide	$\text{Cd} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Cd(OH)}_2$	1.35	5.52	181
Silver-zinc	Zn	AgO	$\text{Zn} + \text{AgO} + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{Ag}$	1.85	3.53	283
Nickel-zinc	Zn	Ni oxide	$\text{Zn} + 2\text{NiOOH} + 2\text{H}_2\text{O} \rightarrow 2\text{Ni(OH)}_2 + \text{Zn(OH)}_2$	1.73	4.64	215
Nickel-hydrogen	H <sub>2</sub>	Ni oxide	$\text{H}_2 + 2\text{NiOOH} \rightarrow 2\text{Ni(OH)}_2$	1.5	3.46	289
Nickel-metal hydride	MH‡	Ni oxide	$\text{MH} + \text{NiOOH} \rightarrow \text{M} + \text{Ni(OH)}_2$	1.35	6.50	206§
Silver-cadmium	Cd	AgO	$\text{Cd} + \text{O} + \text{H}_2\text{O} \rightarrow \text{Cd(OH)}_2 + \text{Ag}$	1.4	4.41	227
Zinc/chlorine	Zn	Cl <sub>2</sub>	$\text{Zn} + \text{Cl}_2 \rightarrow \text{ZnCl}_2$	2.12	2.54	394
Zinc/bromine	Zn	Br <sub>2</sub>	$\text{Zn} + \text{Br}_2 \rightarrow \text{ZnBr}_2$	1.85	4.17	239
Lithium/manganese dioxide	Li	MnO <sub>2</sub>	$\text{Li} + \text{Mn}^{\text{IV}}\text{O}_2 \rightarrow \text{Mn}^{\text{IV}}\text{O}_2(\text{Li}^+)$	3.5	3.50	286
Lithium/iron disulfide	Li(Al)	FeS <sub>2</sub>	$2\text{Li(Al)} + \text{FeS}_2 \rightarrow \text{Li}_2\text{FeS}_2 + 2\text{Al}$	1.73	3.50	285
Lithium/iron monosulfide	Li(Al)	FeS	$2\text{Li(Al)} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} + 2\text{Al}$	1.33	2.99	345
Sodium/sulfur	Na	S	$2\text{Na} + 3\text{S} \rightarrow \text{Na}_2\text{S}_3$	2.1	2.65	377
Sodium/nickel chloride	Na	NiCl <sub>2</sub>	$2\text{Na} + \text{NiCl}_2 \rightarrow 2\text{NaCl} + \text{Ni}$	2.58	3.28	305
Fuel cell						
H <sub>2</sub> /O <sub>2</sub>	H <sub>2</sub>	O <sub>2</sub> (or air)	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	1.23	0.336	2975

\*See Table 6.2 in Chap. 6 for practical values.

† Based on active anode and cathode materials only, including O<sub>2</sub> (electrolyte not included).

‡ MH = metal hydride.

§ Based on 1.2% hydrogen storage (by weight).



## Energy density of Practical Batteries

e.g. C/LiCoO<sub>2</sub> Li 2차전지 (최대방전 용량 1400 mAh, 평균작동전압 3.7 V, 중량 43 g, 부피 15.154 cm<sup>3</sup>)

i) 중량당 에너지 밀도: 얼마나 가벼운 전지를 만들 수 있는가?

$$(1.4 \text{ Ah} \times 3.7 \text{ V}) / 0.043 \text{ kg} = 125.6 \text{ Wh/kg}$$

ii) 최적당 에너지밀도: 얼마나 작은 전지를 만들 수 있는가?

$$(1.4 \text{ Ah} \times 3.7 \text{ V}) / 15.154 \text{ cm}^3 (= 0.015154 \text{ l}) = 356 \text{ Wh/l}$$

TABLE 6.2 Characteristics of Major Battery Systems<sup>a</sup>

Battery system	Anode	Cathode	Practical battery		
			Nominal voltage, V	Energy density†	
				Wh/kg	Wh/L
Primary					
Leclanché	Zn	MnO <sub>2</sub>	1.5	85	165
Magnesium	Mg	MnO <sub>2</sub>	1.7	100	195
Alkaline-MnO <sub>2</sub>	Zn	MnO <sub>2</sub>	1.5	125	330
Mercury	Zn	HgO	1.3	100 <sup>c</sup>	470 <sup>c</sup>
Mercad	Cd	HgO	0.9	55 <sup>c</sup>	230 <sup>c</sup>
Silver oxide	Zn	Ag <sub>2</sub> O	1.6	120 <sup>c</sup>	500 <sup>c</sup>
Zinc/air	Zn	O <sub>2</sub> (air)	1.5	340 <sup>c</sup>	1050 <sup>c</sup>
Li/SO <sub>2</sub>	Li	SO <sub>2</sub>	3.0	260	415
Li/SOCl <sub>2</sub>	Li	SOCl <sub>2</sub>	3.6	320	700
Li/MnO <sub>2</sub>	Li	MnO <sub>2</sub>	3.0	230	550
Li(CF) <sub>n</sub>	Li	(CF) <sub>n</sub>	3.0	220	410
Li/FeS <sub>2</sub>	Li	FeS <sub>2</sub>	1.6	240	500
Solid electrolyte	Li	I <sub>2</sub> (P2VP)	2.8	200–300	700–970
Reserve					
Cuprous chloride	Mg	CuCl	1.3	60	80 <sup>d</sup>
Zinc/silver oxide	Zn	AgO	1.5	30	75 <sup>e</sup>
Thermal	Li	FeS <sub>2</sub>	2.0	40 <sup>f</sup>	100 <sup>f</sup>
Secondary (rechargeable)					
Lead-acid	Pb	PbO <sub>2</sub>	2.0	35	70
Edison	Fe	Ni oxide	1.2	30	55
Nickel-cadmium	Cd	Ni oxide	1.2	35	80
Nickel-metal hydride	(MH)	Ni oxide	1.2	50	175
Silver-zinc	Zn	AgO	1.5	90	180
Nickel-zinc	Zn	Ni oxide	1.6	60	120
Nickel-hydrogen	H <sub>2</sub>	Ni oxide	1.2	55	60
Silver-cadmium	Cd	AgO	1.1	55	100
Zinc-air	Zn	O <sub>2</sub> (air)	1.5	150	160
Zinc/bromine	Zn	Br <sub>2</sub>	1.6	70	60
Lithium-ion	C	Li <sub>x</sub> CoO <sub>2</sub>	4.0	90	200
Lithium-organic	Li	MnO <sub>2</sub>	3.0	120	265
Lithium-polymer	Li	V <sub>6</sub> O <sub>13</sub>	3.0	200	350
High temperature	Li(Al)	FeS <sub>2</sub>	1.7	180	350
High temperature	Na	S	2.0	170	250

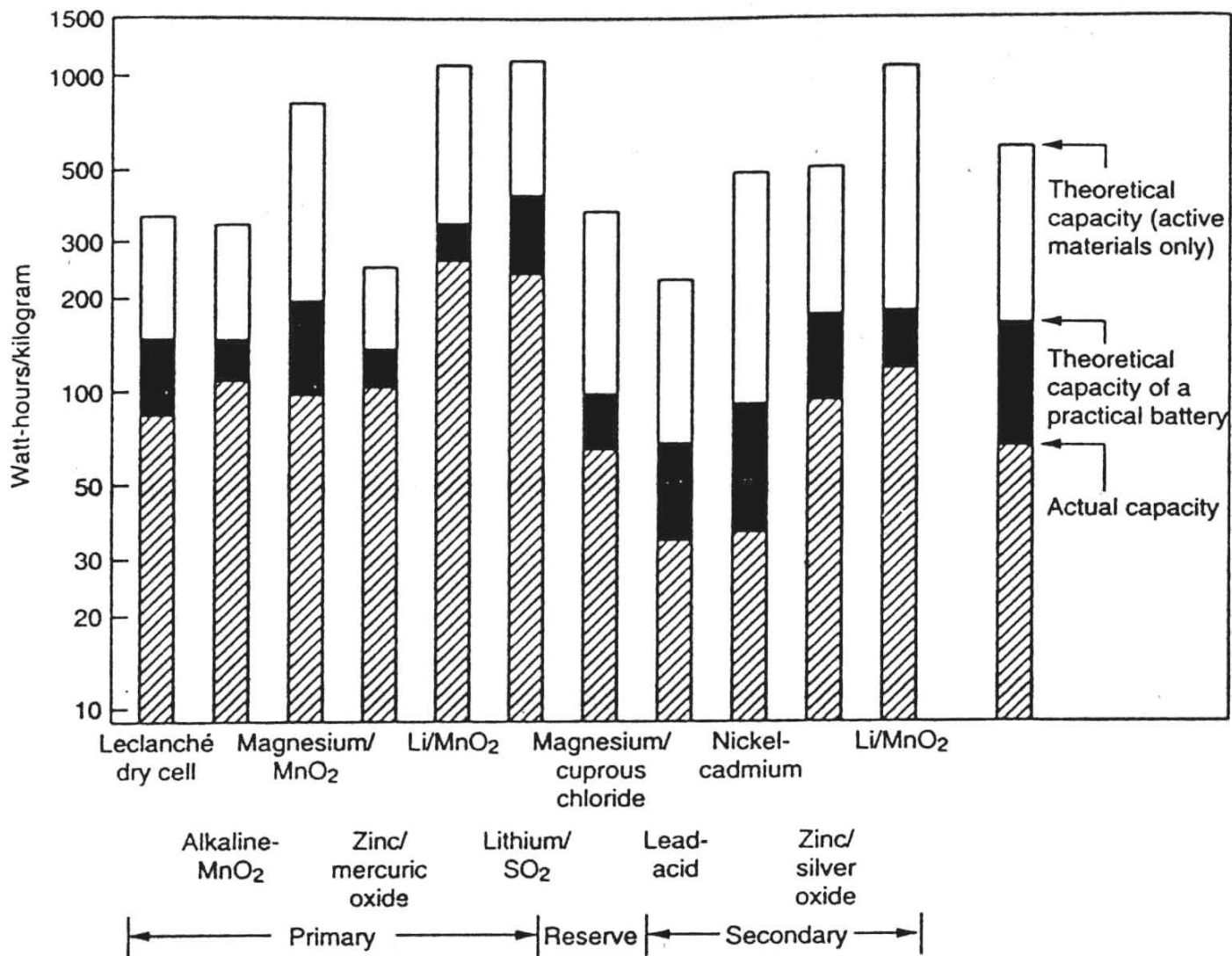


FIGURE 3.3 Theoretical and actual capacity of battery systems.

## 2차전지 효율

i) Coulometric efficiency

$$q_{Ah} = Q_{\text{discharge}}/Q_{\text{charge}}$$

For LIB: 95-100%

ii) Energy efficiency (percent)

- the difference between the energy required to charge a secondary battery and the energy delivered by the battery in use ( $q_{wh} = q_{Ah} \times V_{\text{discharge}}/V_{\text{charge}}$ )

iii) current efficiency (percent)

- the ratio between the quantity of electricity obtained from a battery and that used to charge it

## Cycle life

- a rechargeable battery should be able to be discharged partially or completely, then be recharged, and this should be feasible an infinite number of times → practically not: not the same electrode, electrolyte, separator after charge-discharge cycles, irreversibility in the electrochemical reaction
- **보통 초기용량의 60-80% 수준까지의 총방전 회수. 초기용량의 일정 % 시점과 그때의 용량값 명시. DOD (Depth of Discharge)**

## Rate Performance

-discharge rate: the discharge rate is, as is current, a measure of the rate at which charge is drawn from the cell. It is normally quoted as the “C/n or n-hour rate, which is the current to discharge the nominal capacity C of the battery in n hours.

e.g., 300 mAh capacity battery: 300 mA in 1 h “C-rate”

C/5-rate, 5 h discharge

-Rate performance가 좋으면 상업화 가능성이 더 크다. (예: C-rate에서 95% 방전 > 60% 방전)

## Economics of batteries

- i) Shelf life: self-discharge
- ii) reliability; e.g., pacemaker
- iii) overcharge
- iv) economic & environmental factors

# **Hydrogen Production/Storage**

# Hydrogen Storage

On weight basis: hydrogen has 3 times energy content vs. gasoline  
(120 MJ/kg H<sub>2</sub> vs. 44 MJ/kg gasoline)

On volume basis: 8 MJ/liter H<sub>2</sub> vs. 32 MJ/liter gasoline

## Comparison of storage weight

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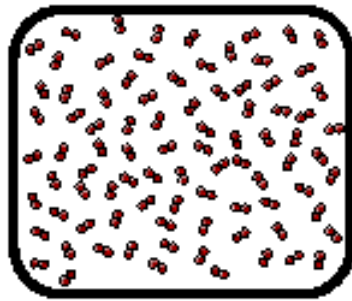
Storage system	Fuel		Tank weight(kg)	Total weight(kg)
	vol(l)	wt(kg)		
Gasoline	30	22	5	27
Compressed H <sub>2</sub>	670	8.2	755	763
Liquid H <sub>2</sub>	115	8.2	65	73
Metal hybrid	-	8.2	764	772

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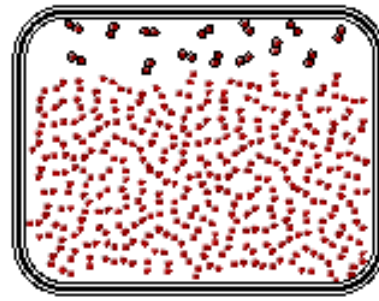
# Hydrogen can be Stored in Different Forms

From DOE

*In tanks ...*



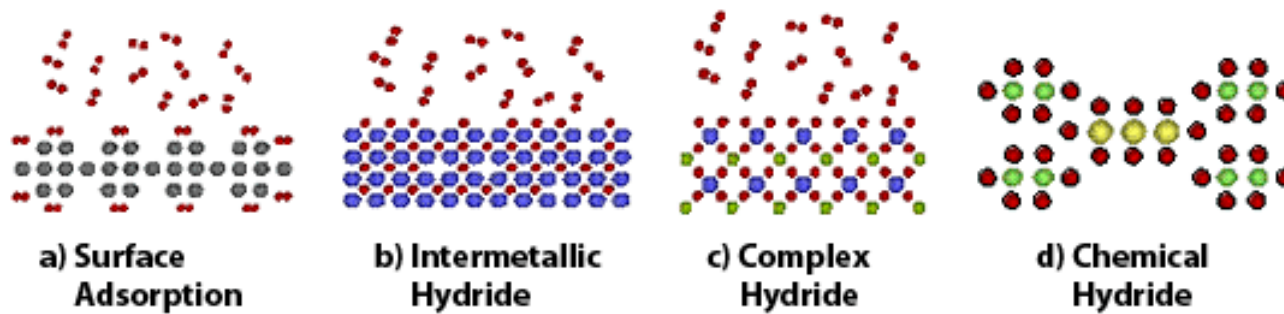
Compressed Gas



Cryogenic Liquid

*and in materials ...*

Hydrogen can be stored on the surfaces of solids by adsorption or within solids by absorption. In adsorption (a) hydrogen attaches to the surface of a material either as hydrogen molecules ( $H_2$ ) or hydrogen atoms ( $H$ ). In absorption (b), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework—this method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms (c).



a) Surface Adsorption

b) Intermetallic Hydride

c) Complex Hydride

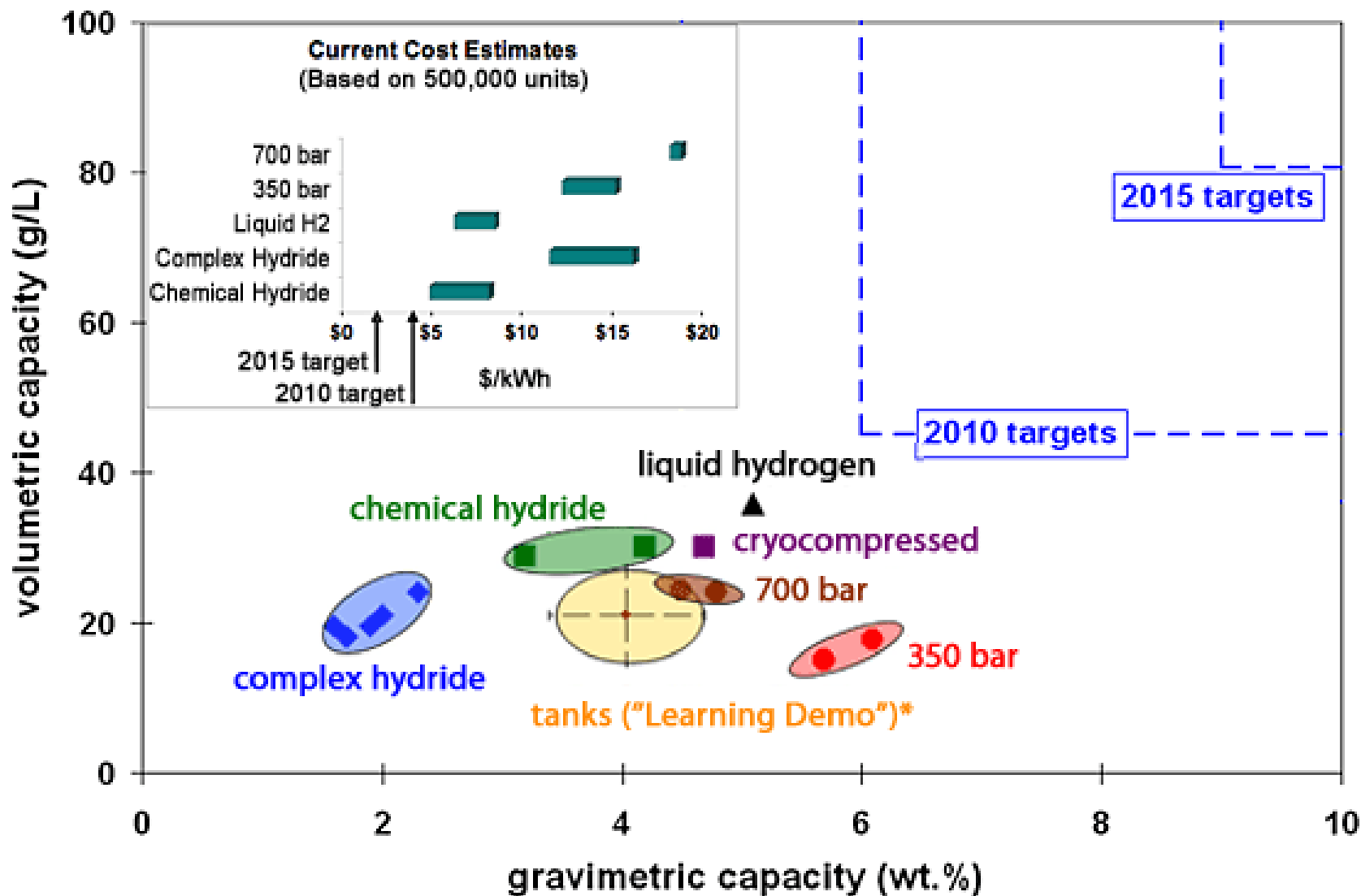
d) Chemical Hydride

Increasing Density →

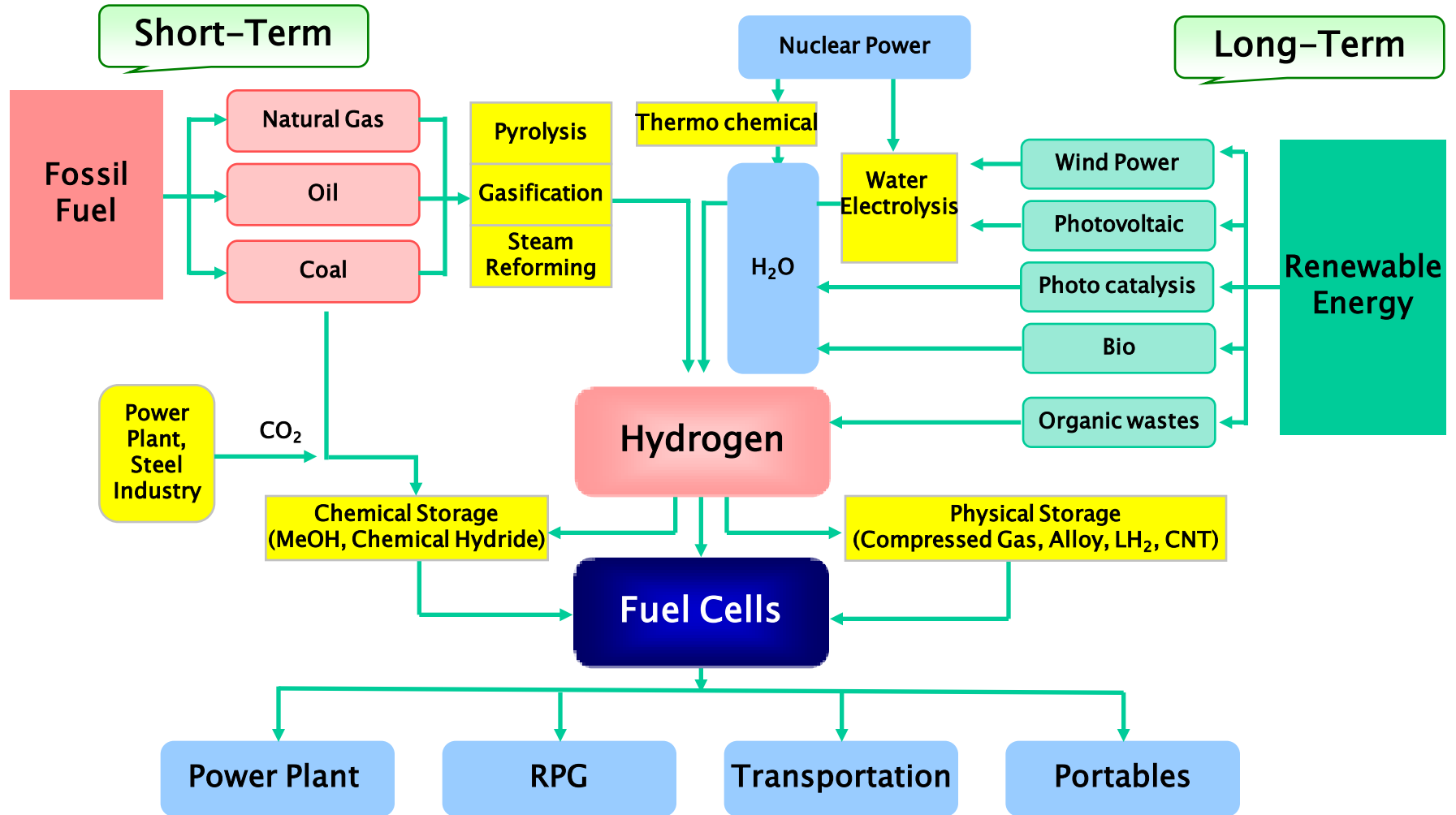
● Hydrogen Atom (H)

●● Hydrogen Molecule ( $H_2$ )





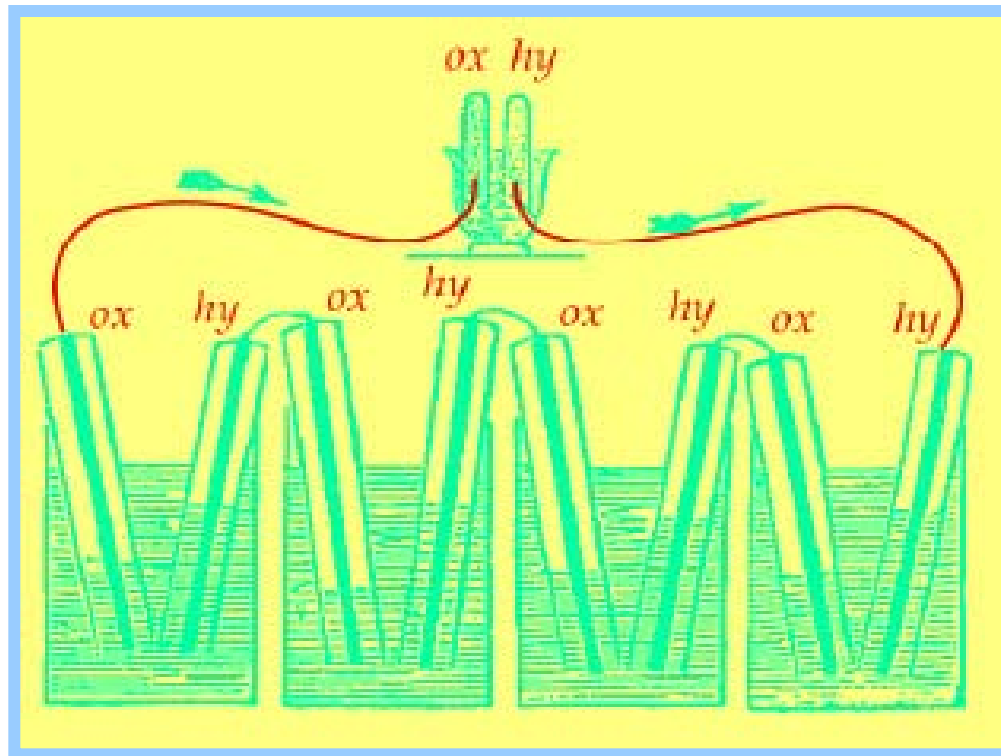
# Hydrogen Economy



# Fuel Cells

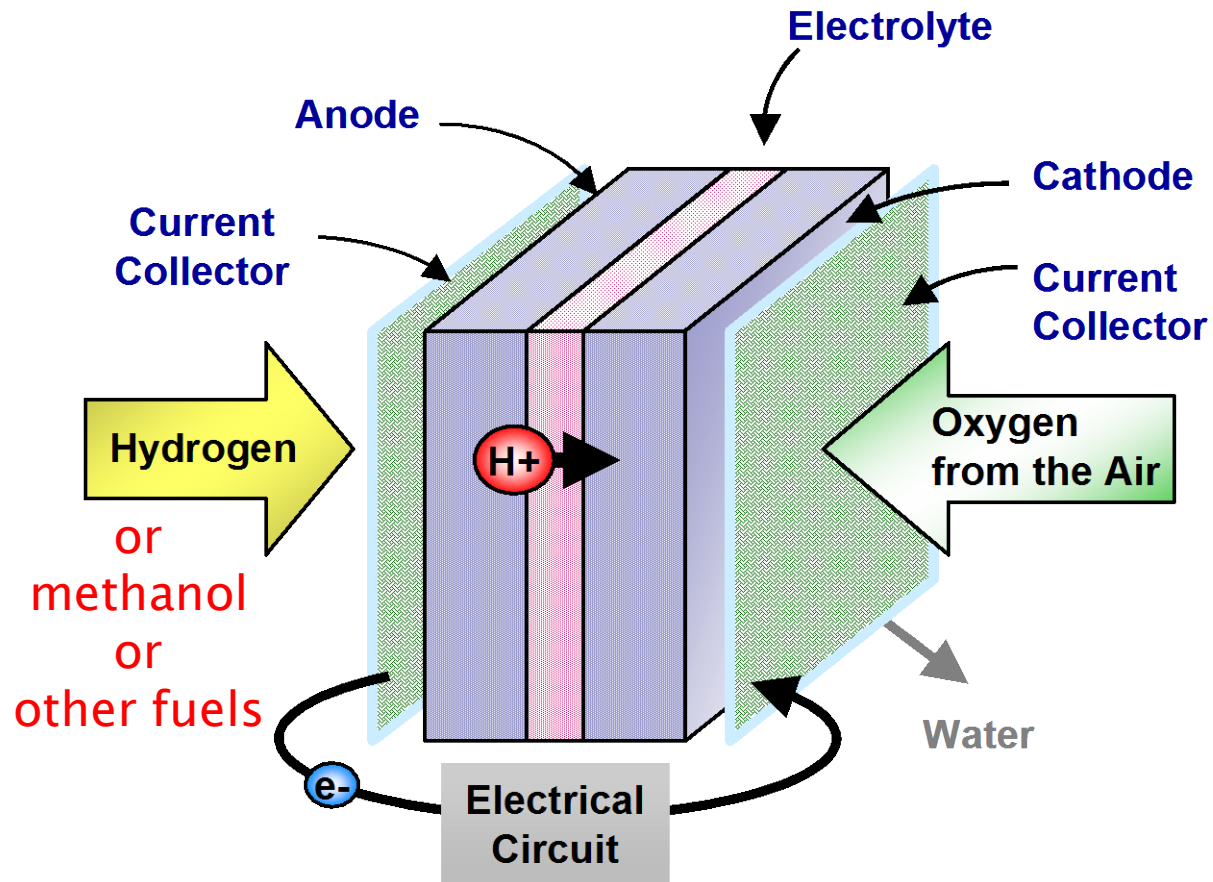
# Brief History

- 1839 Discovery of fuel cell, William Grove
- 1960s Success as power during space flight, NASA
- 1984 Transportation technologies, U.S. Depart. of Energy
- 2000s Portable power sources, Electric company



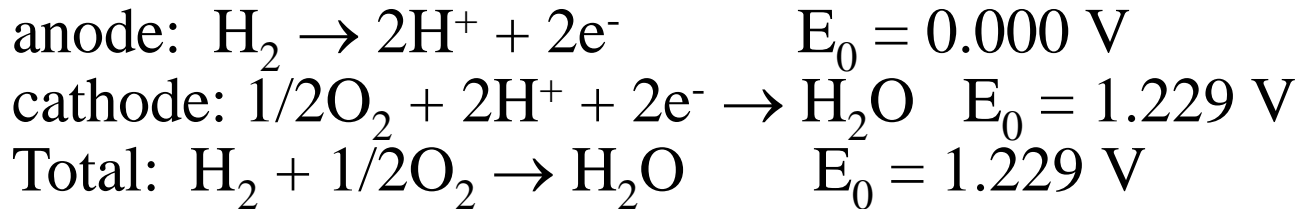
# Fuel Cells

an electrochemical cell which can continuously convert the chemical energy of a fuel and an oxidant to electrical energy

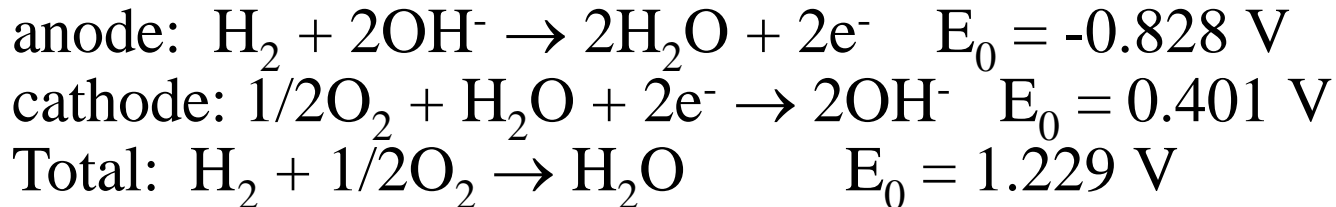


# H<sub>2</sub>-O<sub>2</sub> Fuel Cell reaction

## -In acidic electrolyte



## -In alkaline electrolyte



# 수소-산소 반응의 열역학 및 Kinetics

- Thermodynamics

$$\Delta G = \Delta H - T\Delta S, \quad \Delta G^0 = -RT\ln K$$

K; equilibrium constant,  $\Delta G < 0 \rightarrow$  a reaction can occur  
$$\Delta G = -nFE$$

- Kinetics

– overvoltage or polarization: activation, ohmic, concentration

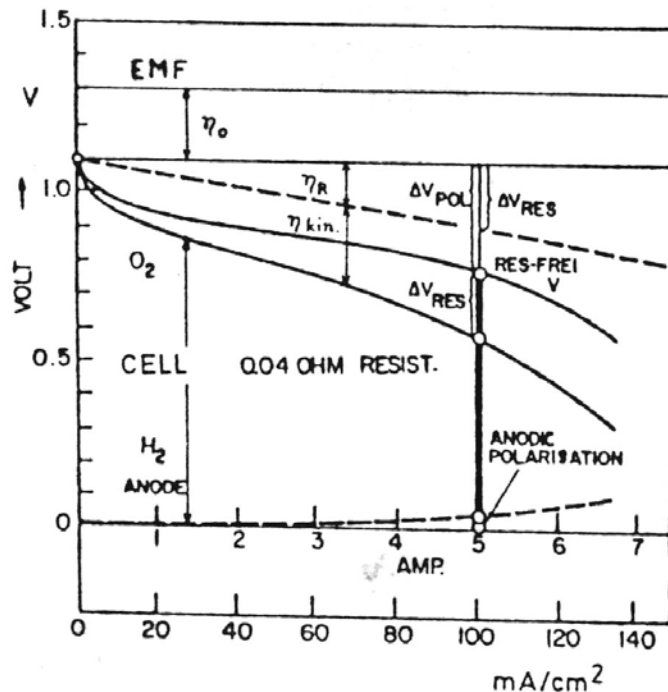
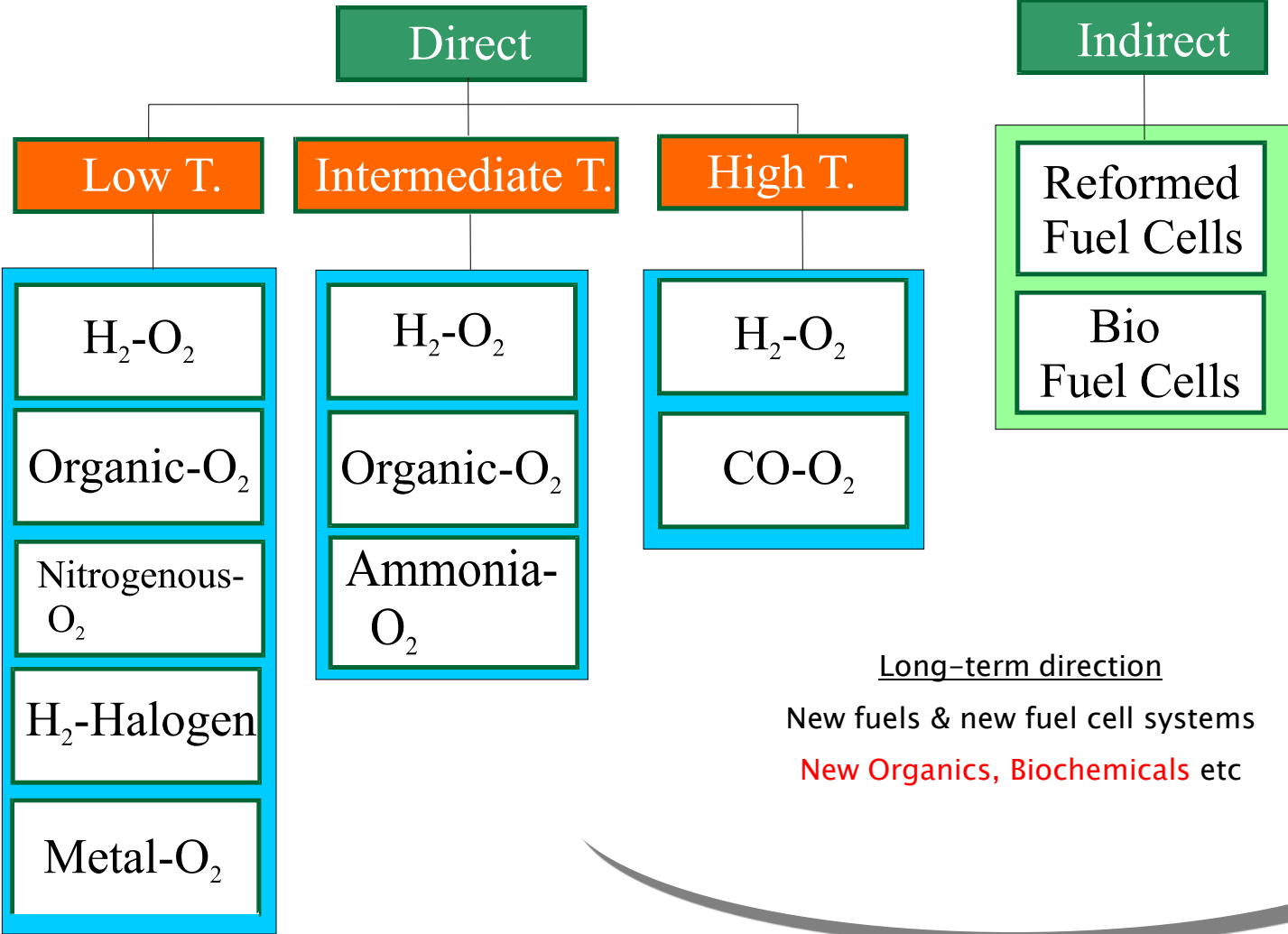


Figure 3-1. Polarization curves of a H<sub>2</sub>-O<sub>2</sub> cell illustrating the components of the cell voltage [4].

# Fuel Cells





# Fuel cell efficiency

- thermodynamic efficiency

$$\eta_{th} = \Delta G/\Delta H = 1 - T\Delta S/\Delta H$$

- typically ~90% ( $H_2 + 1/2O_2 \rightarrow H_2O$ , 83%) to over 100% if the entropy of the products is greater than the entropy of the reactants ( $C + 1/2O_2 \rightarrow CO$ , 124%)

- effect of T;  $\Delta H < 0$ ,  $\Delta S < 0$  (gas  $\rightarrow$  liq)  $\rightarrow$  thermodynamic efficiency  $\downarrow$  as  $T \uparrow$   
cf) high temp; no expensive electrocatalysts needed

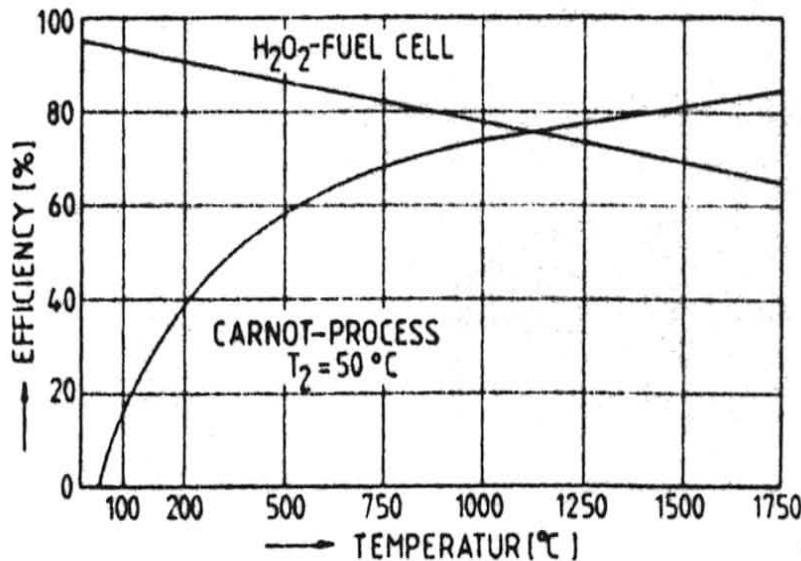


Figure 3-13. Comparison between the Carnot and the Thermodynamic Efficiency of a Fuel Cell

**Table 3-1.** Thermodynamic Data for some Candidate Fuel-Cell Reactions Under Standard Conditions at 25 °C.

Fuel	Reaction	n	$-\Delta H^0$ [kJ/mol]	$-\Delta G^0$ [kJ/mol]	$E^0$ rev. [V]	%
Hydrogen	$\text{H}_2 + 0.5 \text{O}_2 \longrightarrow \text{H}_2\text{O}_{(l)}$	2	286.0	237.3	1.229	83.0
	$\text{H}_2 + \text{Cl}_2 \longrightarrow 2 \text{HCl}_{(aq)}$	2	335.5	262.5	1.359	78.3
	$\text{H}_2 + \text{Br}_2 \longrightarrow 2 \text{HBr}$	2	242.0	205.7	1.066	85.0
Methane	$\text{CH}_4 + 2 \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_{(l)}$	8	890.8	818.4	1.060	91.9
Propane	$\text{C}_3\text{H}_8 + 5 \text{O}_2 \longrightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}_{(l)}$	20	2221.1	2109.9	1.093	95.0
Decane	$\text{C}_{10}\text{H}_{22} + 15.5 \text{O}_2 \longrightarrow 10 \text{CO}_2 + 11 \text{H}_2\text{O}_{(l)}$	66	6832.9	6590.5	1.102	96.5
Carbon monoxide	$\text{CO} + 1.5 \text{O}_2 \longrightarrow \text{CO}_2$	2	283.1	257.2	1.066	90.9
Carbon	$\text{C} + 0.5 \text{O}_2 \longrightarrow \text{CO}$	2	110.6	137.3	0.712	124.2
	$\text{C} + \text{O}_2 \longrightarrow \text{CO}_2$	4	393.7	394.6	1.020	100.2
Methanol	$\text{CH}_3\text{OH} + 1.5 \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_{(l)}$	6	726.6	702.5	1.214	96.7
Formaldehyde	$\text{CH}_2\text{O}_{(g)} + \text{O}_2 \longrightarrow \text{CO}_2 + 2 \text{H}_2\text{O}_{(l)}$	4	561.3	522.0	1.350	93.0
Formic acid	$\text{HCOOH} + 0.5 \text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O}_{(l)}$	2	270.3	285.5	1.480	105.6
Ammonia	$\text{NH}_3 + 0.75 \text{O}_2 \longrightarrow 0.5 \text{N}_2 + 1.5 \text{H}_2\text{O}$	3	382.8	338.2	1.170	88.4
Hydrazine	$\text{N}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{N}_2 + 2 \text{H}_2\text{O}_{(l)}$	4	622.4	602.4	1.560	96.8

- Practical efficiency

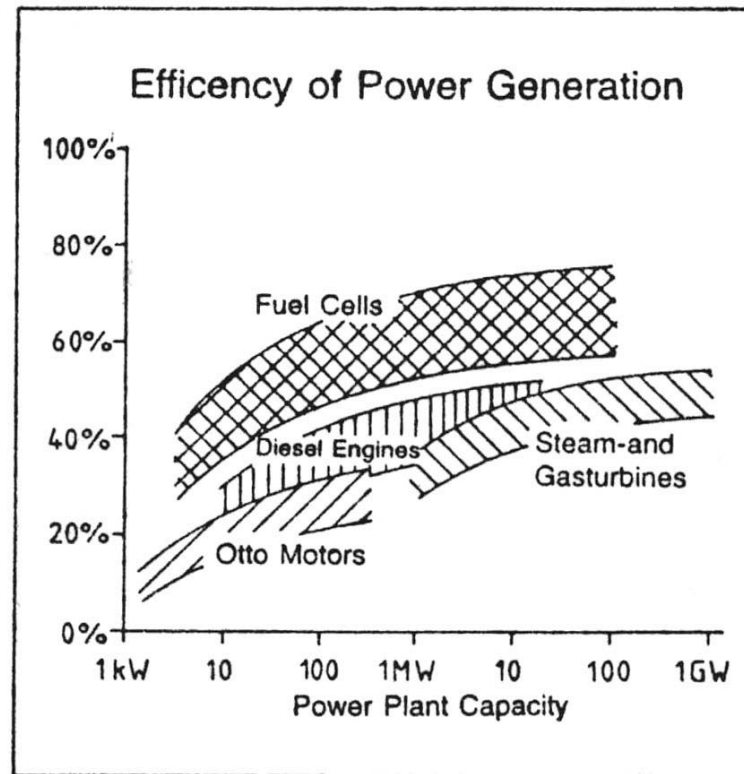
$$\eta_p = -nFE_K/\Delta H$$

$E_K < E_0$ : polarizations

- Faradaic efficiency

$$\eta_f = I/I_m$$

- Total efficiency



## Fuel cell Systems

- classifications; T, P, fuels, electrolytes
- H<sub>2</sub>-O<sub>2</sub> fuel cell types

Fuel Cell System	Temperature ( C )	Efficiency (cell)	Electrolyte	Anode	Cathode	Charge carrier	Fuel
Alkaline Fuel Cell (AFC)	60-90	50-60 %	35-50% KOH	Pt base	Pt base	H <sup>+</sup>	수소
Phosphoric Acid Fuel Cell (PAFC)	160-220	55 %	Phosphoric acid	Pt base	Pt base	H <sup>+</sup>	수소
Molten Carbonate Fuel Cell (MCFC)	620-660	60-65 %	Molten Salts	Ni	NiO	CO <sub>3</sub> <sup>2-</sup>	수소
Solid Oxide Fuel Cell (SOFC)	700-1000	55-65 %	Ceramic	ZrO <sub>2</sub>	Perovskite	O <sup>2-</sup>	수소
Polymer Electrolyte Fuel Cell (PEMFC)	50-80	50-60 %	Polymer Membrane	Pt base	Pt base	H <sup>+</sup>	수소
Direct Methanol Fuel Cell (DMFC)	2 -80	50-60 %	Ion Exchange Membrane	Pt base	Pt base	H <sup>+</sup>	메탄올

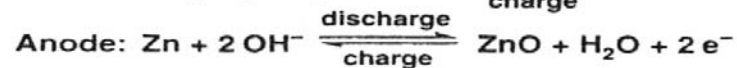
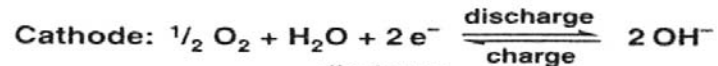
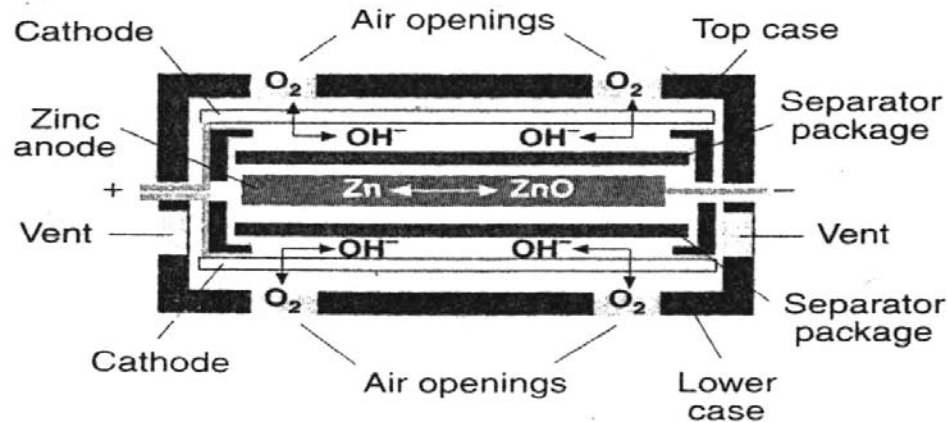
# 연료전지 제품 종류

구분	제품종류 (용량)	연료전지					비고
		PAFC	MCFC	SOFC	PEMFC	DMFC	
대형 발전	지역분산 및 집중 발전 (수십MW 이상)	○	●	●	○	○	
분산 발전	산업용 (수백kW~수십MW)	○	●	●	●	○	
	상업용 (수kW~수백kW)	●	●	●	●	○	
	주거용 (수백W~수kW)	○	○	●	●	○	
수송용	주동력용 (선박용)	○	●	●	●	○	
	주동력용 (승용, 버스)	○	○	●	●	○	
	보조전원용 (수MW~수십MW)	○	●	●	●	○	
	보조전원용 (수kW~수백kW)	○	○	●	●	○	
휴대용	이동전원 (수백W~수kW)	○	○	●	●	●	
	노트북용 (20~수백W)	○	○	○	●	●	
	휴대기기 (5~10W)	○	○	○	○	●	
● : 적용 중    ◐ : 고려 중    ○ : 가능성 적음							

# Hybrid cells

- intermediate between the galvanic cells & fuel cells; advantage of both battery & fuel cells
- metal-air batteries

## Zinc-air cells draw $O_2$ from air to fuel electrochemical reaction



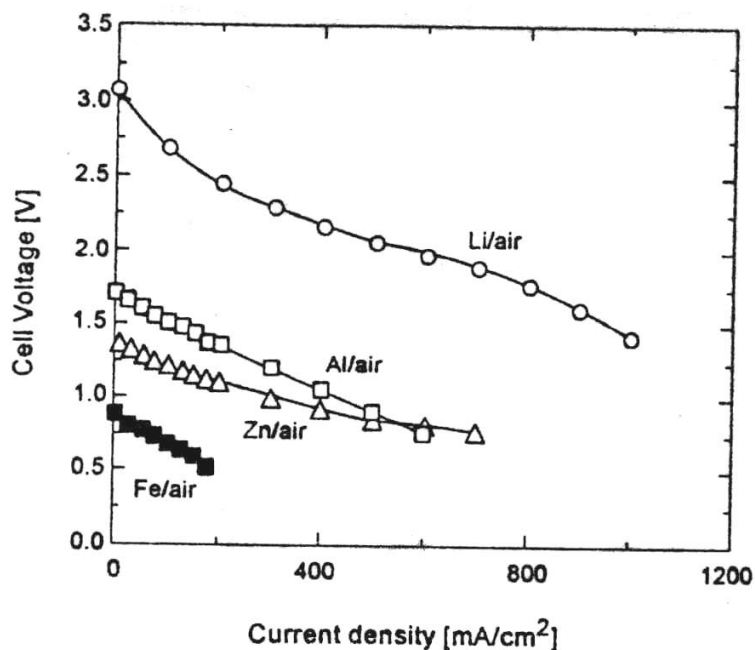
Part battery and part fuel cell, a rechargeable Zn-air cell's cathode catalytically converts ambient  $O_2$  to  $OH^-$  during discharge while a zinc anode is converted to ZnO. When recharging, the reverse reaction occurs.

**Table 4-16. Comparison of Metal/Air Batteries**

Metal Anode	Electrochemical Equivalent of Metal [Ah/g]	Theoretical Cell Voltage* [V]	Valence Change	Theoretical Specific Energy (of Metals) [Wh/g]	Practical Operating Voltage [V]
Li	3.86	3.4	1	13	2.4
Ca	1.34	3.4	2	4.6	2.0
Mg	2.20	3.1	2	6.8	1.4
Al	2.98	2.7	3	8.1	1.6
Zn	0.82	1.6	2	1.3	1.2
Fe**	0.96	1.3	2	1.2	1.0

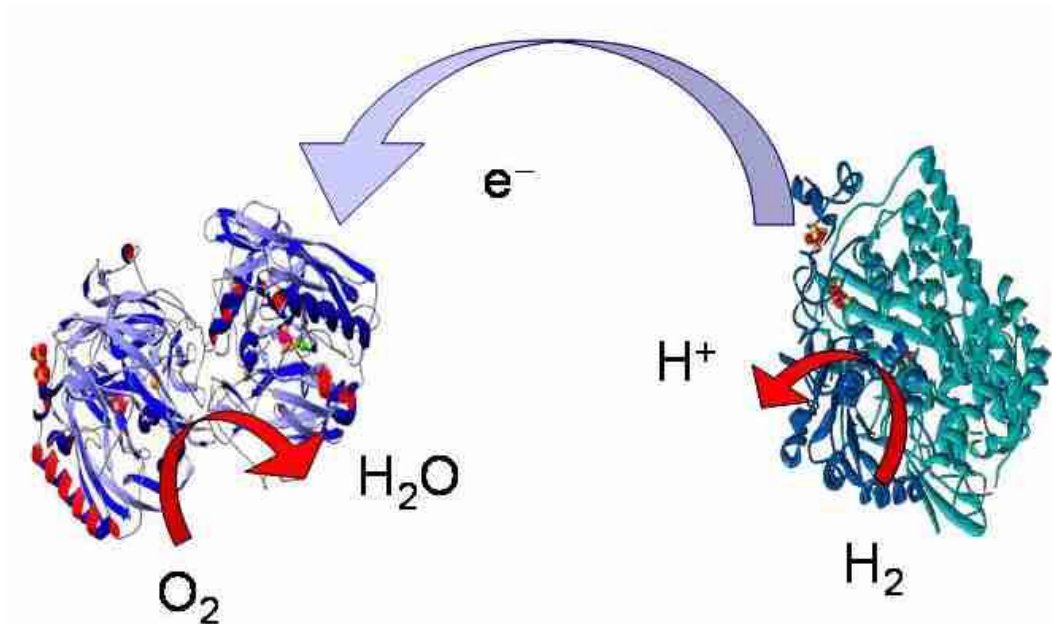
\* Cell voltage with oxygen cathode

\*\*  $\text{Fe}^{2+}$  (1.8 Wh/g for  $\text{Fe}^{3+}$ )



# Bio-fuel Cell

“An electro-chemical device in which energy derived from chemical reactions maintained by a continuous supply of chemical reactants is converted to electrical energy by means of the catalytic activity of **living cells and/or their enzymes.**”



전극: enzyme, bacteria...