에너지 저장 시스템 원리
Basic Principles of Energy Storage System

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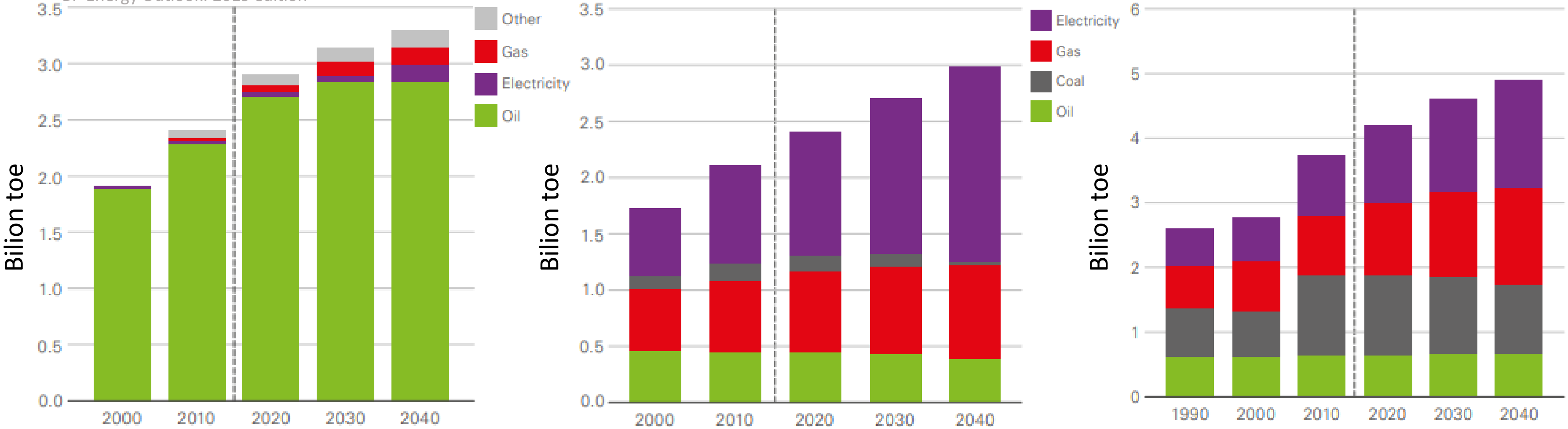
Energy Storage System

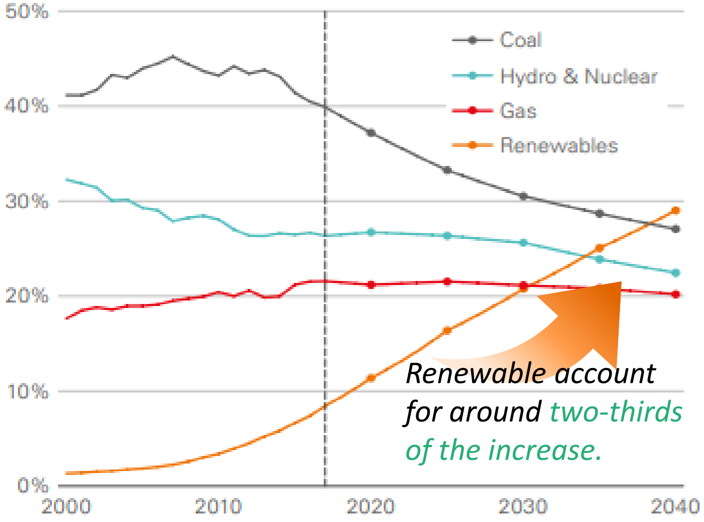
Energy demand and consumption grows by fuel

BP Energy Outlook: 2019 edition



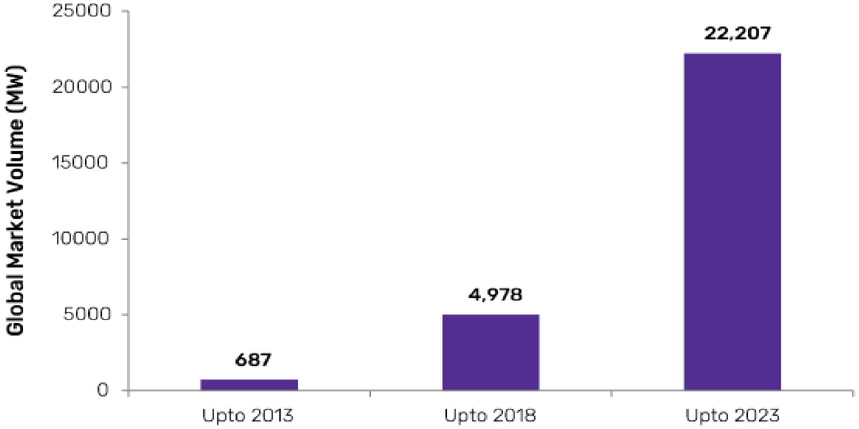
Transport Buidings Industry

Electricity outlook



Renewable account for around two-thirds of the increase.

GlobalData, Power intelligence Center



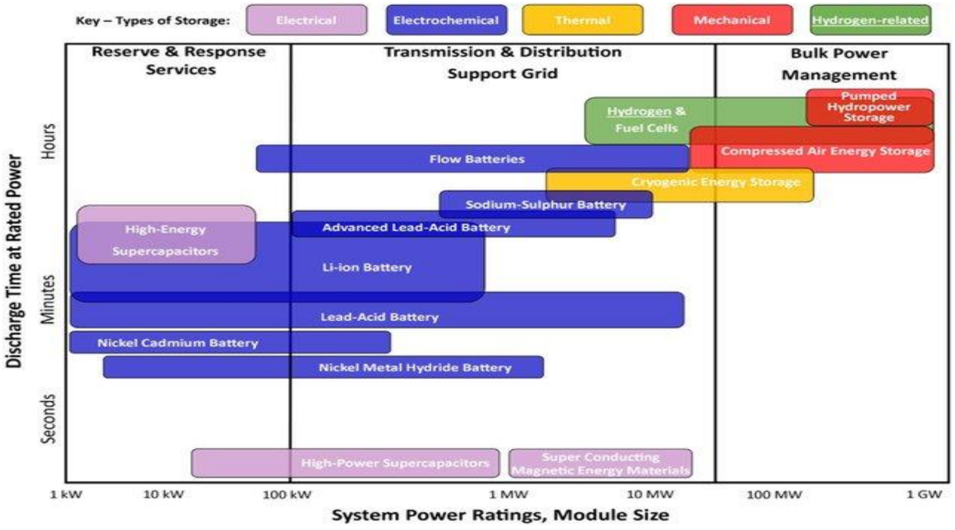
As increasing energy consumption, the energy storage market has caught the eye of a number of stakeholders involved in the power industry, leading to its considerable growth.

Energy Storage System

World Energy Council

Electrical Energy Storage Systems

- Mechanical
  - Pumped hydro storage
  - CAES (compressed air energy storage)
  - LAES (liquid air energy storage)
  - Flywheels
- Thermal
  - Thermo chemical
  - Sensible thermal
  - Latent thermal
- Chemical
  - Hydrogen storage
  - SNG (synthetic natural gas)
- Electro-chemical
  - Li-ion battery
  - Lead acid battery
  - NaS battery
  - Redox flow battery
- Electrical
  - Super capacitor



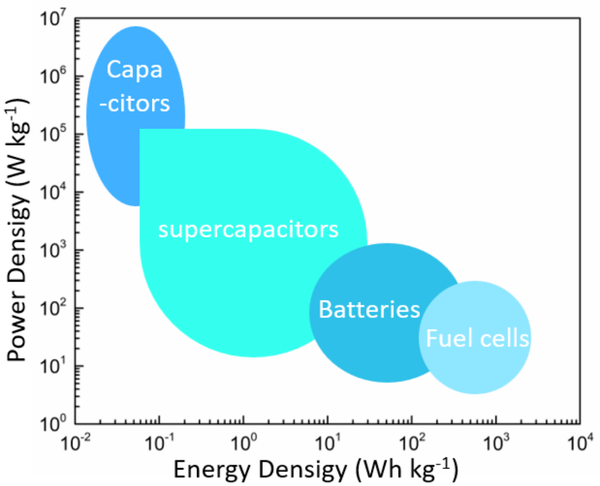
battery → High energy density

Use a charged battery all day

supercapacitor → High power density

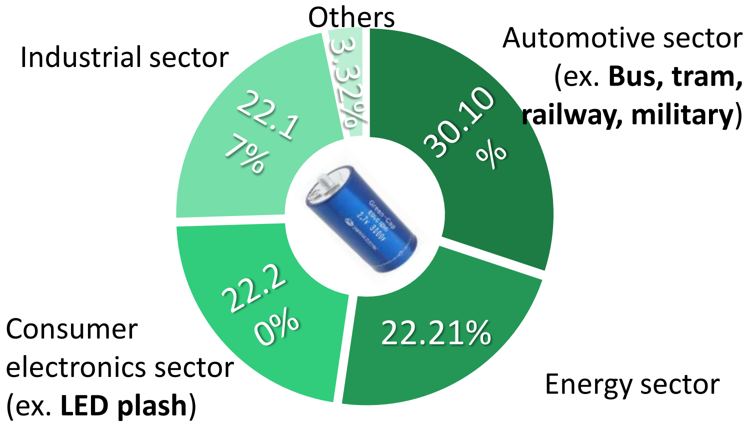
Rapid power delivery and recharging

Supercapacitor



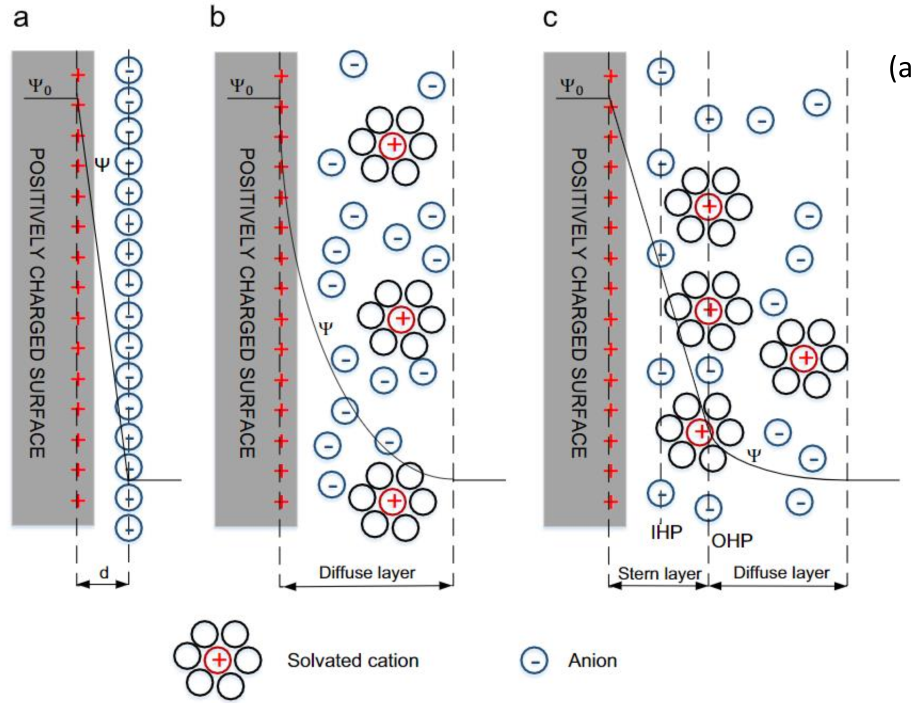
Supercapacitors

- High power density
- High capacitance
- Fast charging ability
- Low temperature
- Long life (15 years)



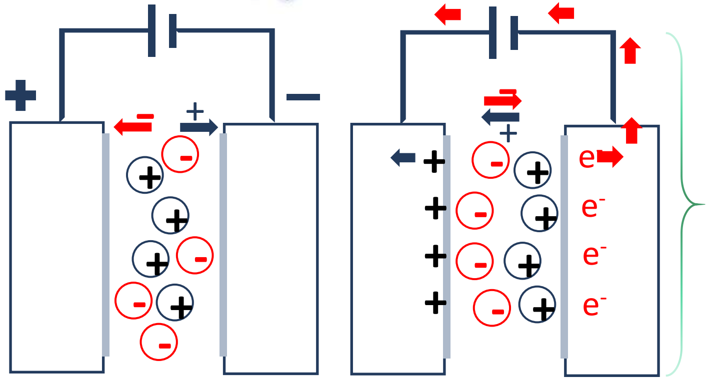
Type of supercapacitor		Electrode material	Charge storage mechanism	Merits/shortcomings
Electrochemical double layer capacitor (EDLC)		Carbon	Electrochemical double layer (EDL), non-Faradaic process	- Good cycling stability - Good rate capability
				- Low specific capacitance - Low energy density
Pseudo capacitor		Redox metal oxide or redox polymer	Redox reaction, Faradaic process	- High specific capacitance - relatively high energy density - relatively high power density
				- Relatively low rate capability
Hybrid capacitor	Asymmetric hybrid	Anode : pseudo capacitance materials	Anode : redox reaction	- High energy density - high power density - good cyclability
		Cathode : carbon(EDLC)	Cathode : EDL	
	Symmetric composite	Redox metal oxide / carbon Redox polymer / carbon	Redox reaction plus EDL	- High energy density - Moderate cost and moderate stability
	Battery-like hybrid	Anode : Li-insertion material	Anode : Lithiation/delithiation	- High energy density - High cost and requires electrode material capacity match
		Cathode : carbon	Cathode : EDL	

Electrochemical double layer capacitor (EDLC)



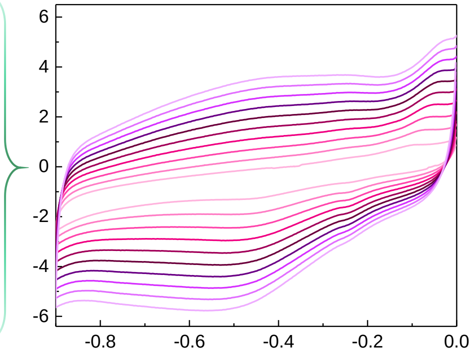
(a) Helmholtz model (b) Gouy-chapman model (c) Stern model

- An electric double layer is a structure appearing when a charged object is placed into a liquid.
- The balancing counter charge for this charged surface will form on the liquid, concentrating near the surface.
- There are several theories or models for this interface between a solid and a liquid.
  ψ : potential
  ψ_0 : electrode potential
  IHP : inner Helmholtz plane
  OHP : outer Helmholtz plane
  explained in the Stern model.



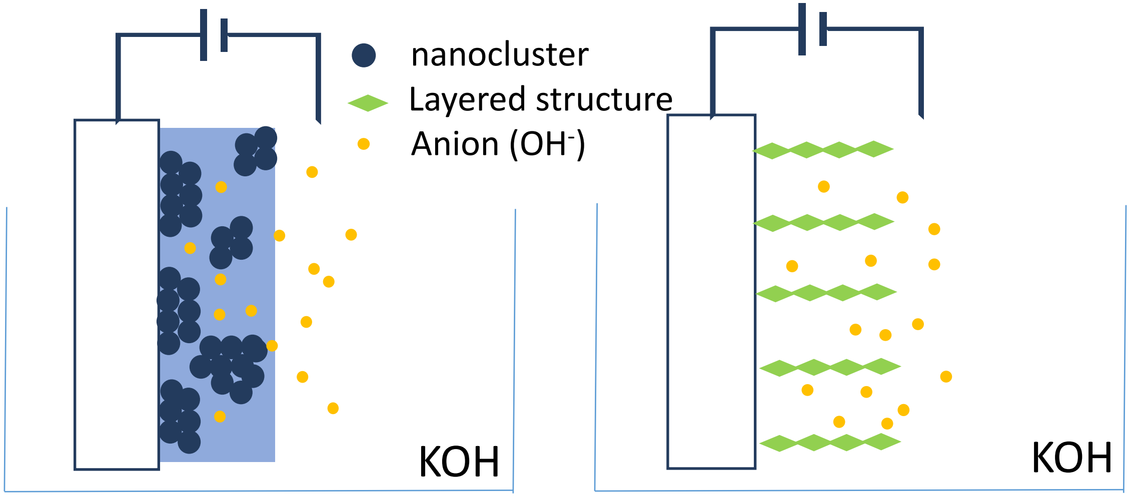
charging

discharging



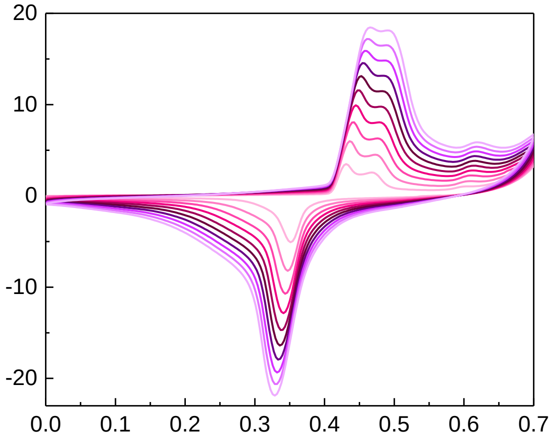
- **Non faradaic process**
- Stores charge electrostatically at electrode/electrolyte interface as charge separation
- There is no charge transfer between electrode and electrolyte
- Intrinsically high power devices(short response time), limited energy storage, very high cycling stability(~10^6)
- Different forms of high surface area carbon are used as an electrode material(Activated carbon, Carbon aerogels, Carbon nanotubes,…)

Pseudo capacitor



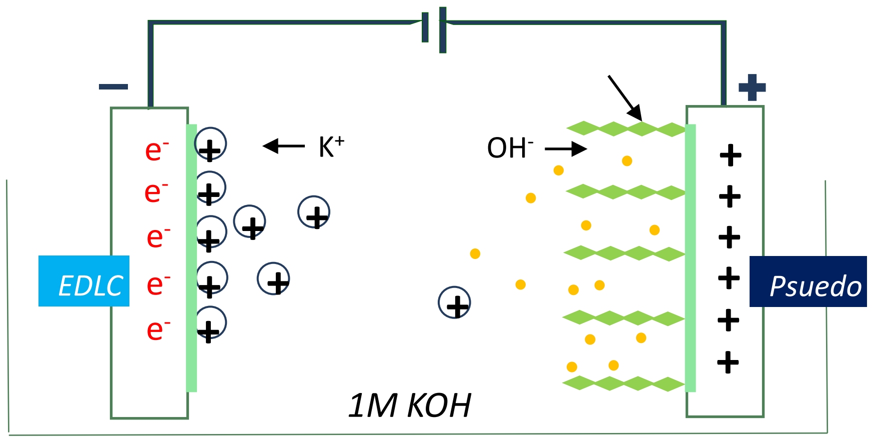
Redox reaction

Intercalation



- Pseudocapacitance is a **Faradaic charge storage mechanism based on fast and highly reversible surface or near-surface redox reactions.**
- The electrical response of a pseudocapacitive material is ideally the same as the one of a double layer capacitor, the state of charge changes continuously with the potential, leading to proportionality constant that can be formally considered as capacitance.
- Some materials can also store a significant charge in a double layer such as functionalized porous carbons, combining thus both capacitive and pseudocapacitive storage mechanisms.
- **Faradic processes occurring together with EDL charge** storage increase the specific capacitance of an electrode.
- The capacitance of a pseudocapacitor can be 10-100 times higher than that of an EDLC.
- Nevertheless, the power performance of a pseudocapacitor is usually lower than that of EDLSCs, due to the slower Faradic processes involved.

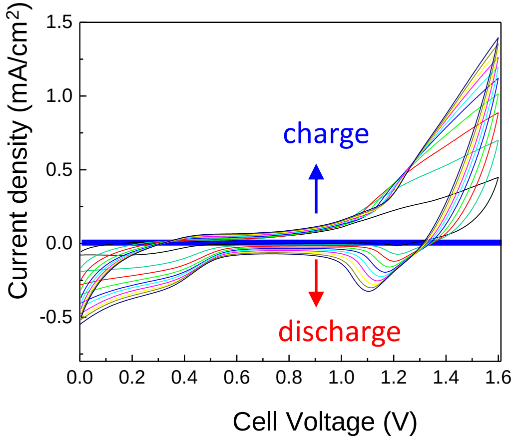
Hybrid Supercapacitor



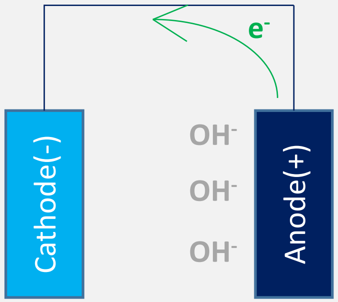
- *One electrode acts as EDLC forming a double layer at the Electrode/Electrolyte interface*
- *Another Electrode acts as Psuedo capacitor involving transfer of charge between Electrode and Electrolyte by Redox Reaction*

◆ Advantage of Hybrid SC

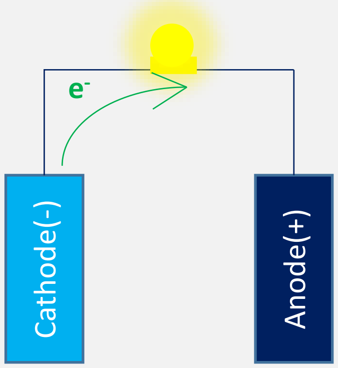
- *High Cyclic life*
- *High Power Density and Energy Density*
- *High Specific Capacity*



How much do you charge electrons?
→ oxidation @ anode

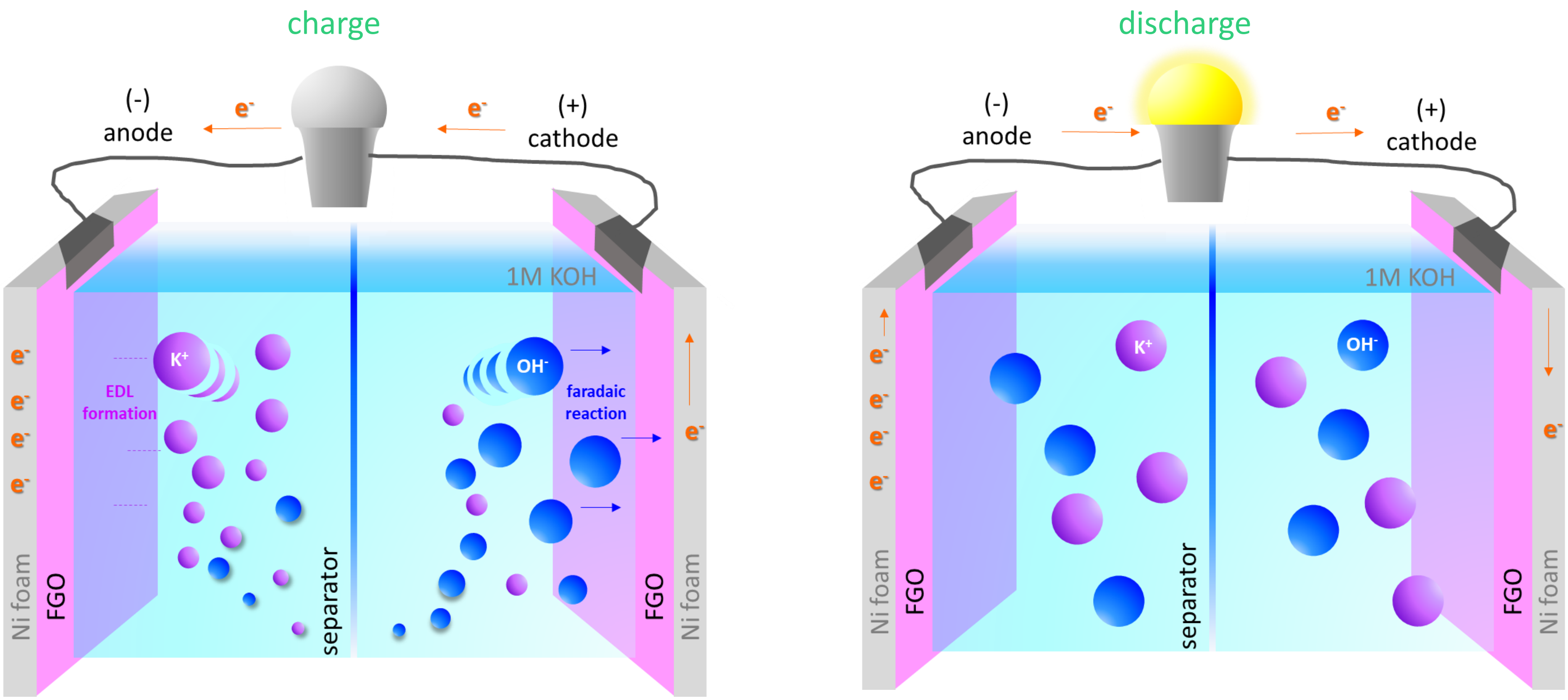


How much do you discharge electrons?
→ reduction @ anode



Supercapacitor Mechanism

Supercapacitor reaction



Calcuation for verifying own capacity at each reaction

$$C_s = \frac{I\Delta t}{m\Delta V}$$

Specific capacitance (F/g)

$$C_S = \frac{I\Delta t}{m}$$

Specific capacity (C/g)

Calcuation for verifying full device capacitance

$$\mathrm{E} = \frac{I\int_0^t V(t)\,dt}{3600 \times m}$$

Energy density (Wh/kg)

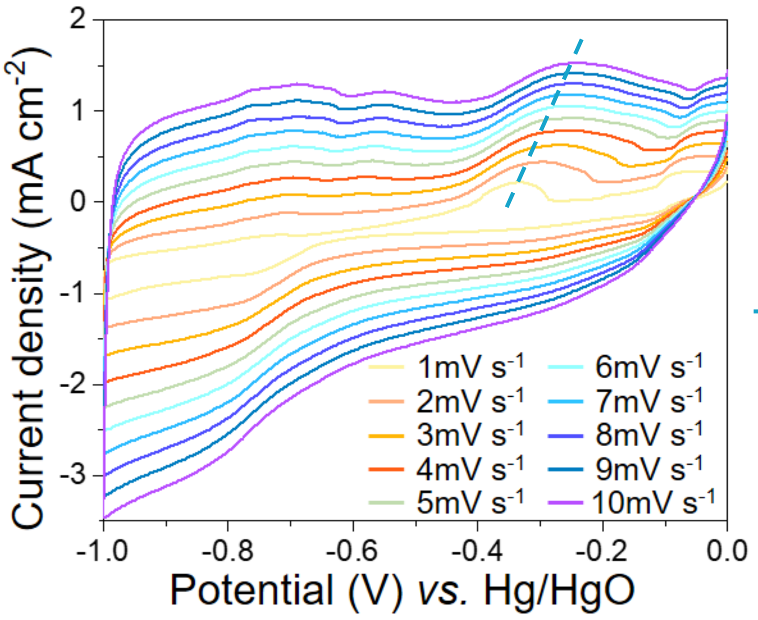
$$\mathrm{P} = \frac{E}{\Delta t}$$

Power density (W/kg)

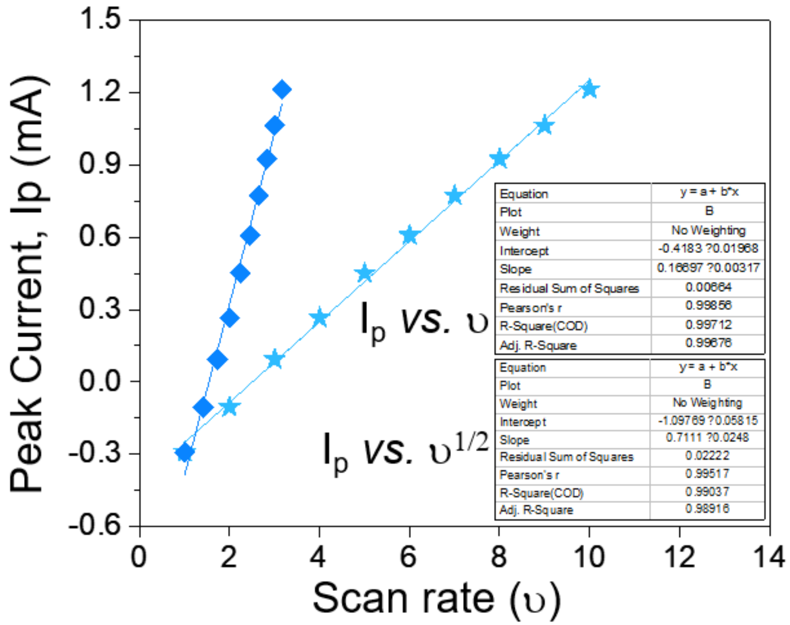
I : current density (mA/cm^2), t: times (sec), m: loading mass (mg), V: applied potential (v)

Calculation Method for Confirming Mechanism

peak current



Peak current *vs.* scan rate



Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-0.4183 ?0.01968
Slope	0.16697 ?0.00317
Residual Sum of Squares	0.00664
Pearson's r	0.99856
R-Square(COD)	0.99712
Adj. R-Square	0.99676

Equation	y = a + b*x
Plot	B
Weight	No Weighting
Intercept	-1.09769 ?0.05815
Slope	0.7111 ?0.0248
Residual Sum of Squares	0.02222
Pearson's r	0.99517
R-Square(COD)	0.99037
Adj. R-Square	0.98916

I_p *vs.* υ

- Linear: electrochemical double layer capacitor (EDLC)
- Non-linear: pseudo capacitor

I_p *vs.* $υ^{1/2}$

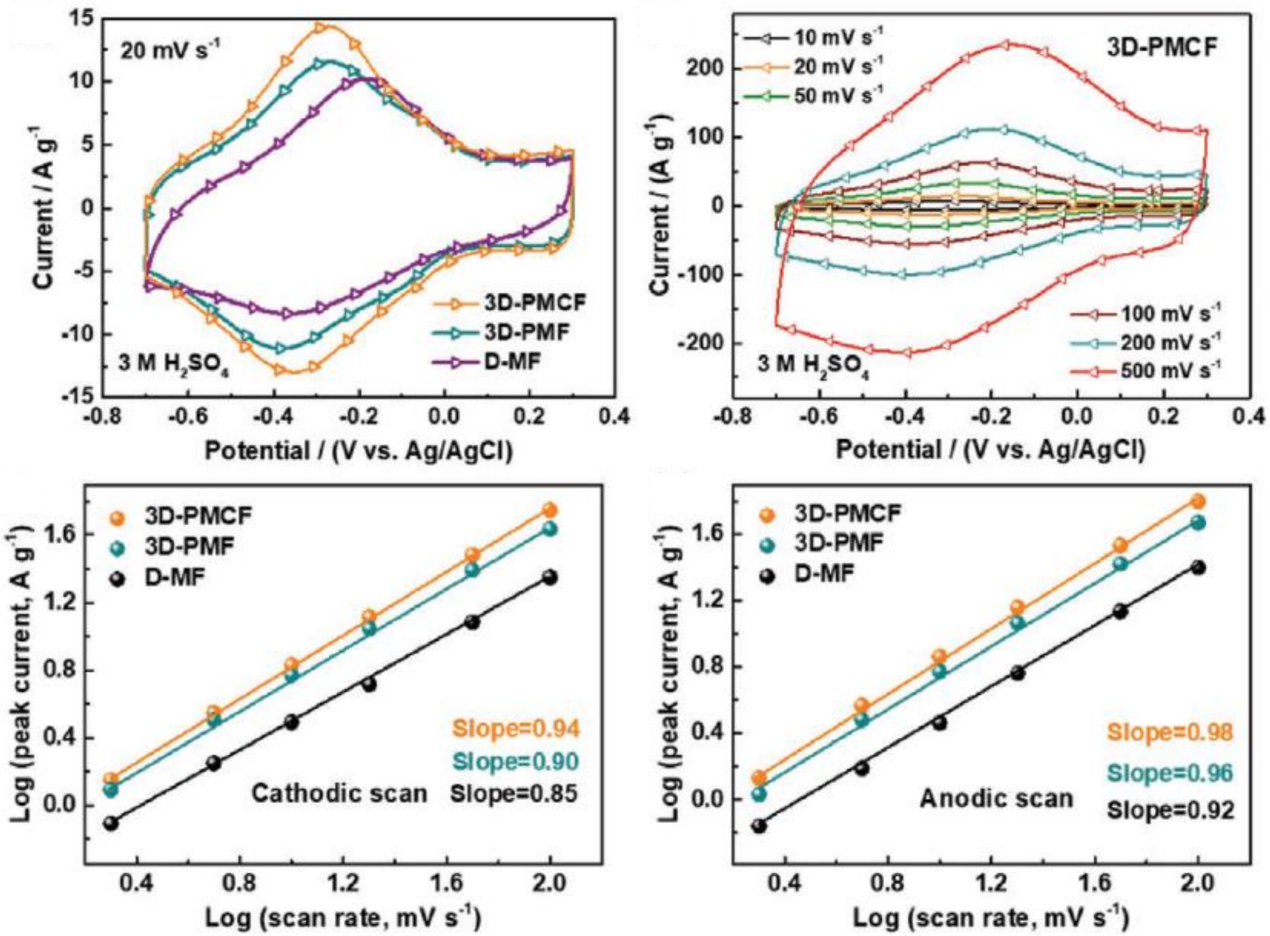
- Linear: pseudo capacitor
- Non-linear: electrochemical double layer capacitor (EDLC)

I_p: peak current, υ: scan rate

Calculation Method for Confirming Mechanism

b-value from power law

Adv. Funct. Mater. **2020**, 2000922



$i = a\upsilon^{b} \longrightarrow \log(i) = b\log(\upsilon) + \log(a)$

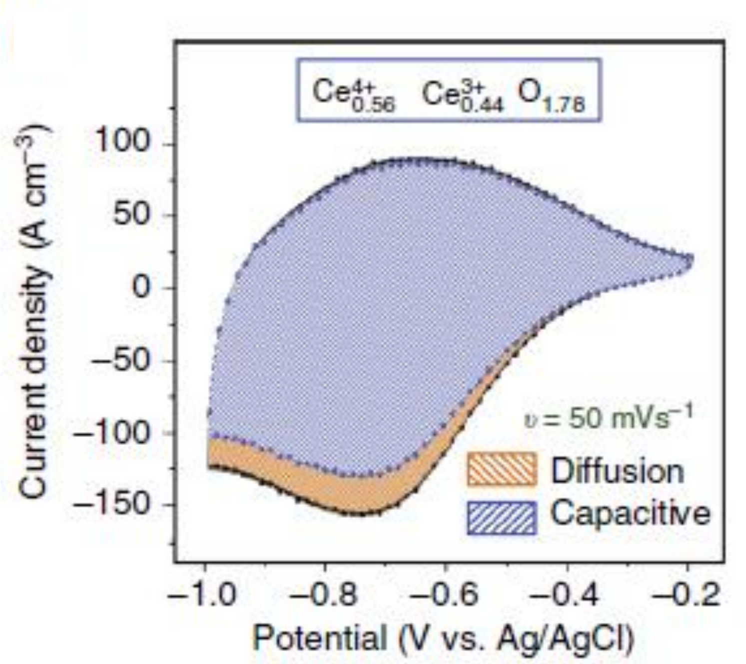
i: peak current, υ: scan rate

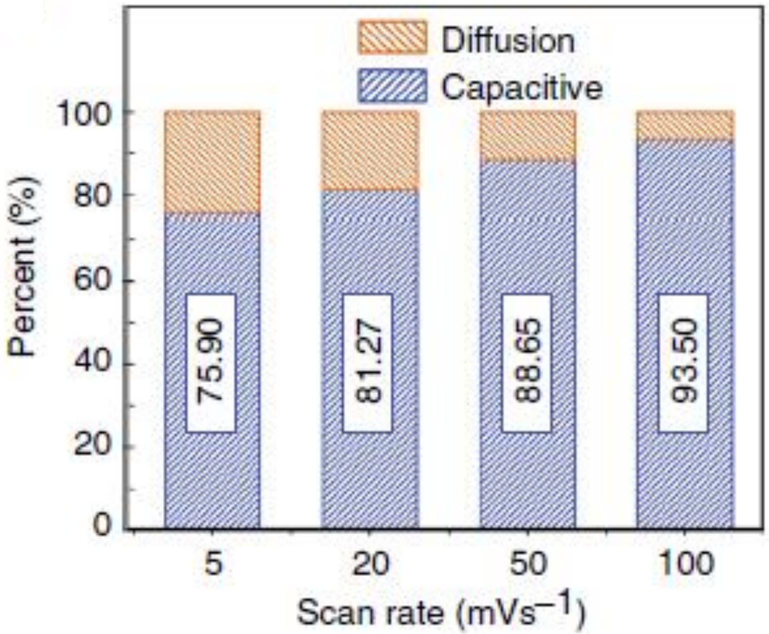
- b-value
  ~0.5: pseudo behavior
  ~1.0: EDLC behavior

Calculation Method for Confirming Mechanism

total contribution of capacitive and diffusion

Nature communications, 2019, 10.1: 1-9.





$$\frac{i}{v^{0.5}}(y) = k_1 \frac{v}{v^{0.5}}(x) + k_2 : \textit{linear fittng}$$

i: peak current, υ: scan rate

K_1: EDLC, K_2: pseudo

- EDLC part of CV
  $i = k_1 \upsilon$
- pseudo part of CV
  $i = k_2 \upsilon^{0.5}$
- Total CV
  $i = k_1 \upsilon + k_2 \upsilon^{0.5}$

Electrochemical Battery

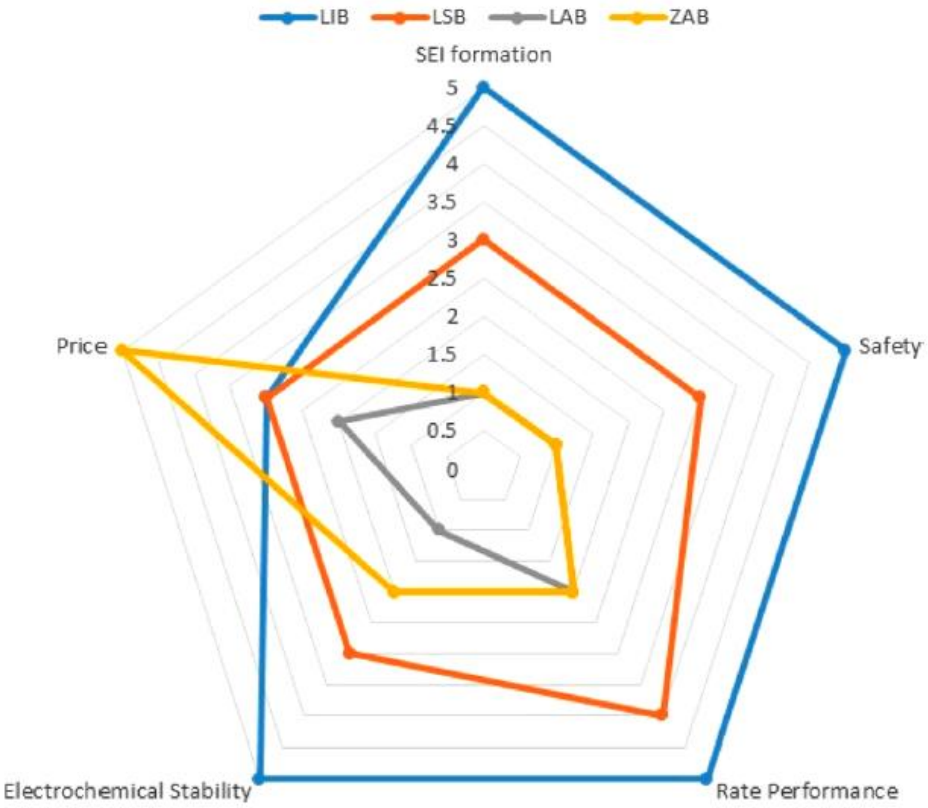
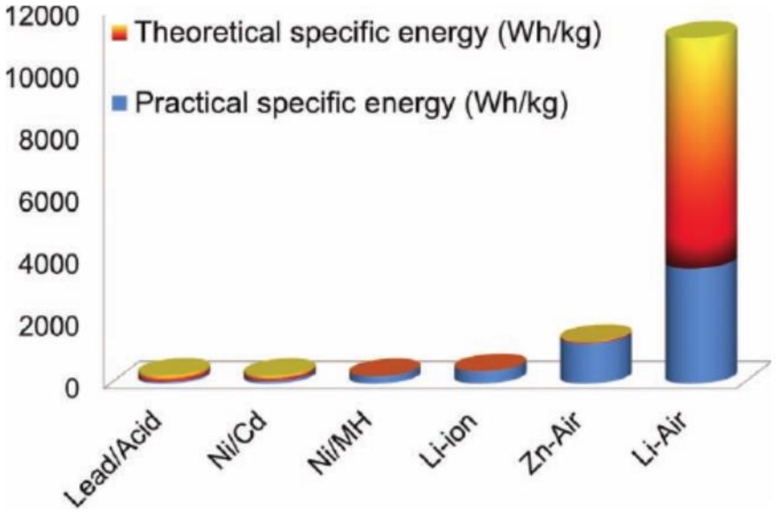


Figure 1. SOA electrolytes for four energy storage technologies ranked by their SEI formation, safety, price, rate performance, and electrochemical stability.

LI, Matthew, et al. New Concepts in Electrolytes. Chemical Reviews, 2020.

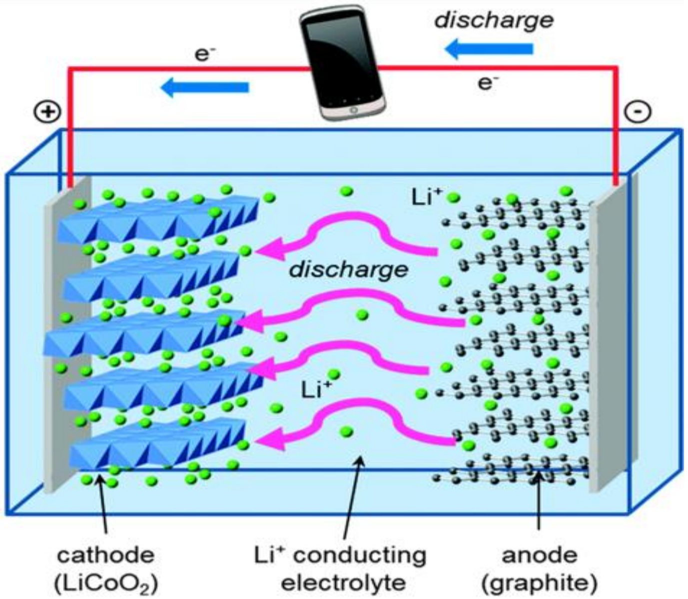
Lee, J. S., and Jaephil Cho. Advanced Energy Materials, (2011)



Secondary Batteries	Theoretical Specific energy density (Wh/kg)	Practical Specific Energy Density (Wh/kg)
Li-Ion	387	~160
Li-Air	~13,000	~1,700
Zn-Air	~1,300	~350
Li-Sulfur	~2,600	~370

Electrochemical Battery

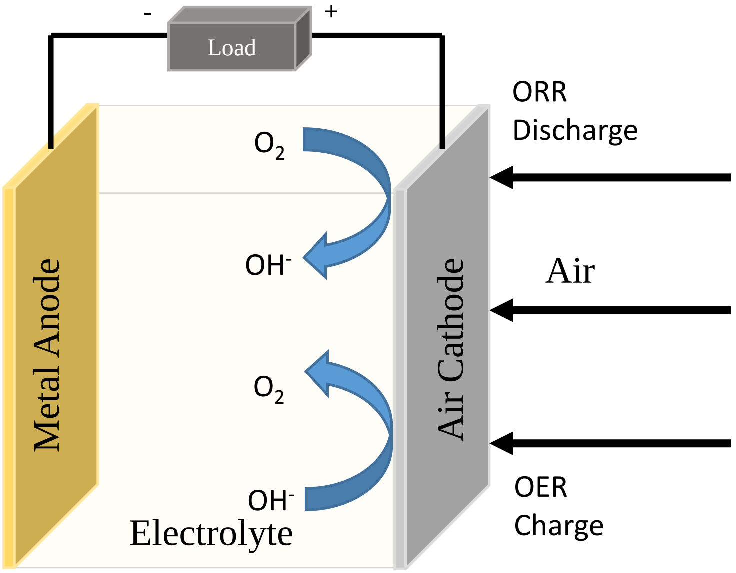
Intercalation/Insertion-type Electrode



ex) $Li^+ + CoO_2 \Leftrightarrow LiCoO_2$

- The ions are inserted in /deserted out from layered(spinel) structure
- Key component/mechanism in Ion Batteries

Conversion-type Electrode



ex) $M^+ + O_2 \Leftrightarrow MO_2$ (M = Metal)

- The ions are converted to other form through electrochemical reactions
- Key component/mechanism in Metal-Air, Lithium-Sulfur Batteries

Zn-Air Battery

Batteries	Limitations
Aluminum-Air	Formation of Alumina (Al_2O_3); Considered more as Primary Battery (Electrochemically)
Magnesium-Air	Formation of passivating layer, slow kinetics
Iron-Air	Formation of Iron Oxide (FeO); causing rapid sintering and pulverization

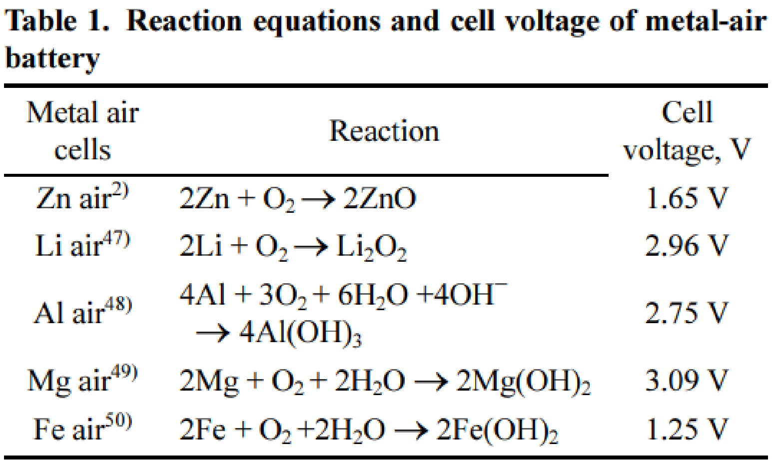


Table 1. Reaction equations and cell voltage of metal-air battery

Metal air cells	Reaction	Cell voltage, V
Zn air[2)]	$2Zn + O_2 \rightarrow 2ZnO$	1.65 V
Li air[47)]	$2Li + O_2 \rightarrow Li_2O_2$	2.96 V
Al air[48)]	$4Al + 3O_2 + 6H_2O + 4OH^- \rightarrow 4Al(OH)_3$	2.75 V
Mg air[49)]	$2Mg + O_2 + 2H_2O \rightarrow 2Mg(OH)_2$	3.09 V
Fe air[50)]	$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$	1.25 V

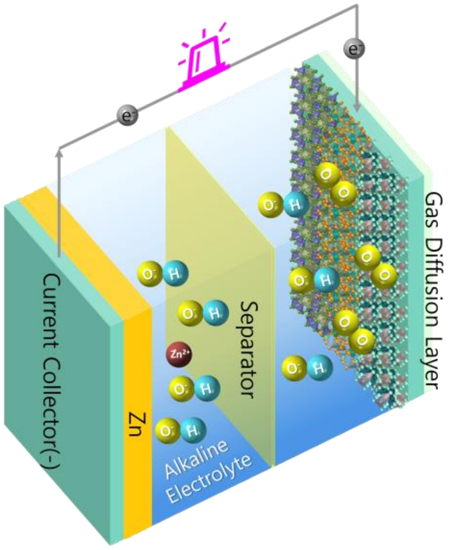
Ryu, S. K. and Jin-Soo Park, Journal of the Korean Electrochemical Society, (2013)

Li-air battery

- Better Reversibility
- High Operating Potential
- High Capacity → High Energy Density

Zn-air battery

- Stable towards moisture
- Price Competitiveness
- Closer to Practical Applications



While the difference rely on the metal anodes, the key compartment of the Metal-Air battery systems is the cathode.