



Modeling, Management and Application of Lithium-Ion Battery Energy Storage Systems



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Agenda

- Battery Mechanism & Operating Principles;
- Battery Management Systems;
- Battery Modeling and Characterization;
- Future Development.



Battery



The first battery was invented by Alessandro Volta in 1800: : Zn-Cu



Example: PbA Battery

Discharging Negative Plate:

Positive Plate:

Overall:

 $Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^-$

 $PbO_2 + HSO_4^- + 3H^+ + 2e \rightarrow PbSO_4 + 2H_2O$

 $PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$





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Example: PbA Battery

Overall:	$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$					
Charge	2e-					
Mass	239 207 196					
Relative mass: Pb: 207 O:16 S: 32	Other info: 1. One electron: -1.602*10 ⁻¹⁹ C 2. One hydrogen atom: 1.667*10 ⁻²⁷ kg					

To transfer Q=2*1.602*10⁻¹⁹C charge, we need the mass M= $(239+207+196)*1.667*10^{-27}$ kg, yielding Q/M/3600=83Ah/kg



Li-ion Battery Inventions

2019 Nobel Prize in Chemistry: development of lithium-ion batteries



John B. Goodenough M. Stanley Whittingham Akira Yoshino 1980s battery positive material 1972 1st Li battery 1980s 1st Li-ion Battery CURENT

Li-ion Battery History



Lithium-metal Battery(Primary)

In 1972, Whittingham (Exxon): TiS₂ (Low voltage, layered-type structure)+ Li metal

Early 1980s, Goodenough proposed the families of compounds: Li_xMO_2 (where M is Co, Ni or Mn)



Rechargeable Li-ion battery (Secondary)

Started in 1981 and invented in 1985, Yoshino: substitute metallic Li for a second insertion material (carbon-rich anode, socalled Li-ion or rocking-chair technology)

1991, Sony commercialized C/LiCoO₂ (3.6V, 120-150 Wh/kg)



J.M. Tarascon, M. Armand, Issue and challenges facing rechargeable lithium batteries, Nature, 414(2001)359

Li-ion Battery





Li-ion Battery Structure



Anode: 90-95% active material, 3-5% conductive carbon, 3-5% binder, 25-30% porous, 25-90 microns thick depending on intended battery characteristics



Li-ion Battery Structure



Optical microscope image



Morphology of Battery Materials



Carbonaceous spheres (graphite, negative electrode)



Lithium manganese oxide (positive electrode)













SEM Surface Photomicrograph of Celgard® Monolayer PP Battery Separator





SEM Surface Photomicrograph of Celgard® Monolayer PE Battery Separator

Why Li-ion? (1)

3 Li 6.94	Li Be 94 901 Elements 2005											5 B 10.81	6 C 12.01	7 N 14.01	8 0 15.99	9 F 19.00	10 Ne 20.18
Na 22.99	Mg 25.31	12 12 12 12 13 4 5 6 7 8 9 10 11 12										Al 26.98	Si 28.09	P 30.97	S 32.07	17 Cl 35.45	Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti ^{47.87}	23 V 50.94	24 Cr 52.00	25 Mn ^{54.94}	Fe 55.85	CO 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se _{78.96}	35 79.90	36 Kr ^{83.80}
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb _{92.91}	42 Mo _{95.94}	4.3 TC (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 CS 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 OS 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 200.59	81 T 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 AC (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 HS (270)	109 Mt (268)	110 DS (281)	111 Rg (272)							
58 59 60 61 62 63 64 65 66 67 68 69 7 Molecular 140.12 140.91 144.24 (145) 150.36 151.97 157.25 158.93 162.50 164.93 167.26 168.93 173.00							70 Yb 173.04	71 Lu 174.97									
1	In	stitut	e e	90 Th 232.04	91 Pa ^{231.04}	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 NO (259)	103 Lr (262)

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Why Li-ion? (2)

	Reduction Half-Reaction		E° (V)	
Stronger	$F_2(g) + 2e^- \longrightarrow$	2 F (aq)	2.87	Weaker
oxidizing	$H_2O_2(aq) + 2 H^+(aq) + 2 e^- \longrightarrow$	$2 H_2O(l)$	1.78	reducing
agent	$MnO_4^-(aq) + 8 H^+(aq) + 5 e^- \longrightarrow$	$Mn^{2+}(aq) + 4 H_2O(l)$	1.51	agent
	$Cl_2(g) + 2e^- \longrightarrow$	2 Cl ⁻ (<i>aq</i>)	1.36	
	$\operatorname{Cr}_2\operatorname{O}_7^{2-}(aq) + 14 \operatorname{H}^+(aq) + 6 \operatorname{e}^- \longrightarrow$	$2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2O(l)$	1.33	
	$O_2(g) + 4 H^+(aq) + 4 e^- \longrightarrow$	$2 H_2O(l)$	1.23	
255	$Br_2(l) + 2 e^- \longrightarrow$	2 Br ⁻ (<i>aq</i>)	1.09	
	$Ag^+(aq) + e^- \longrightarrow$	Ag(s)	0.80	
	$Fe^{3+}(aq) + e^{-} \longrightarrow$	$Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2 H^+(aq) + 2 e^- \longrightarrow$	$H_2O_2(aq)$	0.70	
	$I_2(s) + 2 e^- \longrightarrow$	2 I ⁻ (<i>aq</i>)	0.54	
	$O_2(g) + 2 H_2O(l) + 4 e^- \longrightarrow$	4 OH ⁻ (<i>aq</i>)	0.40	
	$Cu^{2+}(aq) + 2e^{-} \longrightarrow$	Cu(s)	0.34	
	$\operatorname{Sn}^{4+}(aq) + 2 e^{-} \longrightarrow$	$\operatorname{Sn}^{2+}(aq)$	0.15	
	$2 H^+(aq) + 2 e^- \longrightarrow$	$H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^{-} \longrightarrow$	Pb(s)	-0.13	
	$Ni^{2+}(aq) + 2e^{-} \longrightarrow$	Ni(s)	-0.26	
	$Cd^{2+}(aq) + 2e^{-} \longrightarrow$	Cd(s)	-0.40	
	$Fe^{2+}(aq) + 2e^{-} \longrightarrow$	Fe(s)	-0.45	
	$Zn^{2+}(aq) + 2e^{-} \longrightarrow$	Zn(s)	-0.76	
	$2 H_2O(l) + 2 e^- \longrightarrow$	$H_2(g) + 2 OH^{-}(aq)$	-0.83	
	$Al^{3+}(aq) + 3e^{-} \longrightarrow$	Al(s)	-1.66	
Weaker	$Mg^{2+}(aq) + 2e^{-} \longrightarrow$	Mg(s)	-2.37	Stronger
oxidizing	$Na^+(aq) + e^- \longrightarrow$	Na(s)	-2.71	reducing
agent	$Li^+(aq) + e^- \longrightarrow$	Li(s)	-3.04	agent

V 0 ag

Example: Li-ion Battery

A fully charged Li-ion battery has positive electrode as CoO₂ and negative electrode as LiC₆

<M> + <HLi> \rightarrow <MLi> + <H>

Here $M = CoO_2$, $\langle HLi \rangle = LiC_6$

Therefore the overall chemical reaction when discharging is

$$CoO_2$$
 + $LiC_6 \rightarrow LiCoO_2$ + $6C$

Relative

mass:

Li: 6.9 Other info:

- Co:59 1. One electron: -1.602*10⁻¹⁹C
 - 2. One hydrogen atom: 1.667*10⁻²⁷kg
- C: 12

O: 16



Example: Li-ion Battery

CoO_2 + LiC_6 \rightarrow $LiCoO_2$ + 6C

Relative mass 59+16*2 6.9+12*6

To generate Q=1.602*10⁻¹⁹C, we need M=169.9*1.667*10⁻²⁷kg. Therefore the gravimetric charge density is Q/M/3600=157Ah/kg.

The energy density is 3.4V*151Ah/kg=534Wh/kg

What are those parameters of the Pb-Acid Battery?

83Ah/kg 174Wh/kg



However...



Why?

Cathode Voltage vs. Degree of Li+ Intercalation C/LiCoO2 Cell



x in Li_xCoO₂



Why?

Electrolyte stability

-Standard commercial Li-ion electrolytes only stable to ~4.5V vs. Li/Li+

• $\text{Li}_{x}\text{CoO}_{2}$ thermodynamic stability $-X = 0.5-1.0 \rightarrow \text{stable compound}$ $-x<0.5 \rightarrow \text{Li}_{x}\text{CoO}_{2} \rightarrow \text{Li}_{2}\text{O/Co}_{2}\text{O}_{3}/\text{Co}_{3}\text{O}_{4}/\text{O}_{2}$



Battery vs Others

- What do I need to Travel 1 mile, in a vehicle?
- 80g of CNG These utilize thermal 96g of Gasoline processes 200g of chocolate 1600g of a lithium-ion cell These utilize 6900g of a lead-acid cell electrochemical processes 20g of lithium metal!

Solid and liquid fuels have much higher energy density than the battery using electrochemical reactions



Solid-state Battery





Li-ion Battery Electrolyte

• Solvent: Blend of organic carbonates

Chemical name	Chemical structure	Viscosity	Dielectric	Melting Point	Flash Point
Ethylene carbonate (EC)	~~ •	(CP) 1.9 (40 °C)	89	37	160
Propylene carbonate (PC)	∽⊸	2.5	65	-49	132
Diethyl carbonate (DEC)	~~~~~	0.75	2.8	-74	31
Dimethyl carbonate (DMC)		0.59	3.1	4.6	18
Ethyl methyl carbonate (EMC)	\sim	0.65	3.9	-53	25
Water		0.88	78	0	Non- flammable

The **flash point** of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air.

Solid-state Battery

Pros:

- High safety: no dendrite piercing through the separator; low flaming possibility;
- High energy density: no need for carbon to collect Li; 300 400Wh / kg;
- Long cycling lifespan: ideally up to 45000 cycles.

Cons:

- High resistance : due to not close contact between solid and solid; slow ion movement in the solid;
- High cost.



Solid-state Battery





Cell, Module and Pack

 The conventional battery pack uses cells to build module and then assembles modules to a pack.

 A blade battery pack builds on wide and short cells and assembles them directly into a pack, thereby having much higher mass and volume integration efficiencies than the conventional pack.

RENT



Yang, XG., Liu, T. & Wang, CY. Thermally modulated lithium iron phosphate batteries for mass-market electric vehicles. Nat Energy 6, 176–185 (2021).

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Cell, Module and Pack



Use the AA Alkaline cells as a starting point – 1.5 V, 2.2 Ah cell

- 1. Series connection increases voltage;
- 2. Parallel connection increases Ah-capacity;
- 3. Combinations increase both voltage and Ah capacity.

Cells



Cell, Module and Pack



Individual Cells



A prismatic Li-ion module by A123 system



Battery Pack by A123 system

Pack vs Cell



- Gravimetric cell-to-pack ratio (GCTP, the ratio of specific energy at the pack level to that at cell level)
- Volumetric cell-to-pack ration (VCTP)

Yang, XG., Liu, T. & Wang, CY. Thermally modulated lithium iron phosphate batteries for mass-market electric vehicles. Nat Energy 6, 176–185 (2021).



Chevrolet Volt battery pack

T shape, 288 LG P1 pouch cell



"Chevrolet Volt Battery Pack Tests, Final Report" Rept. No. GTL-DOT-11-VOLTBAT, 20-Jan-2012, by General Testing Laboratories, Inc., Colonial Beach, Virginia, for USDOT.



Battery Management Systems

An embedded system (purpose-built electronics plus processing to enable a specific application)



1X Master BMS Unit

- Communicates with outside system via CAN 2.0B
- Manages pre-charging and contactors
- Monitors pack voltages

1-64X Monitor BMS Units

- Measures cell voltages and temperatures
- Balances cells
- Communicates with Master BMS via internal data link



STAFL System

Why Managing? (1)

Imbalance in voltage, state-of-charge and temperature among cells

- Reduces the capacity of the battery
- Reduces the lifetime of the battery
- Increases with large charge/discharge cycles



Why Managing? (1)



Kandler Smith, NREL Milestone Report, 2008



Why Managing? (2)

Catastrophic failure rate in commercial Li-ion batteries ~ 1 in 5-10 million •Equates to ~1 in 1 million laptops •BUT also equates to ~1 in 1000 Tesla Roadsters







Why Managing? (2)





BMS Functions

1. Sensing and high-voltage control

• voltage, current, temperature; control contactor, precharge; ground-fault detection, thermal management

2. Protection against

• Over-charge, over-discharge, over-current, short circuit, extreme temperatures

3. Interface

Range estimation, communications, data recording, reporting

4. Performance management

• State-of-charge (SOC) estimation, power-limit computation, balance/equalize cells

5. Diagnostics

• Abuse detection, state-of-health (SOH) estimation, stateof-life (SOL) estimation





Passive Resistor Balancing



- Energy of high-voltage cells is consumed by resistors
- Loss of energy due to balance
- Hard to manage heat
- Can only balance the over-voltage cell



Example: LT Resistor Balancing





Capacitive Balancing



- Slow speed balancing: up to 20 hours
- Large size Capacitor

NT

• Lack of enable/disable feature





Inductive Balancing



Werner Rößler, Boost battery performance with active charge-balancing, Infineon, EE Times India, 2008. http://www.powerdesignindia.co.in/STATIC/PDF/200807/PDIOL_2008JUL24_PMNG_TA_01.pdf?SOURCES=DOWNLOA D

Example: LT Active Balancing





Dynamic Balancing

- The lowest row/cell is charged by the DC-DC converter using the pack voltage
- The highest cell is discharged to the whole pack
- Difficulty is the small duty ratio for large packs



Ziling Nie, and Chunting Mi, "Fast Battery Equalization with Isolated Bidirectional DC-DC Converter for PHEV Applications," the Fifth IEEE International Vehicle Power and Propulsion Conference (VPPC), Dearborn, Michigan, USA, September 7-11, 2009.

Battery Modeling



Simple Model

Simulink, ADVISOR

Middle Model

Physics-Based Model

- 1. Cell geometries, particle sizes, material properties and even particle shape can be varied, in simulation, to optimize a cell's characteristics without the need to build numerous experimental cells
- 2. Connection between battery external properties (SOC) and internal parameters (Li ion concentration)

State of Charge

1C: We define the discharging/charging current using one-hour to deplete/charge the battery from full/empty to empty/full as 1C;

SOC: a proportion of the charge available at that point compared to the total charge available when it is fully charged. Full:100%. Empty: 0%;

In EV, **SOC** evaluation is also known as *fuel gauge* due to its analogy to a gas car's fuel gauge.

Attention: Cell SOC ≠ Battery SOC

Depth of Discharge

DOD: a measure of the charge removed from the battery or cell. DOD could be expressed either in Ah or %.

In most cases: DOD(%) = 1-SOC. This description is not always true.

A battery with 100Ah rated capacity could be further discharged even when its SOC is already 0 (not recommended though). This battery could discharged 105Ah, meaning over discharged. Using DOD(%) = 1-SOC, its SOC = 0% and its DOD is 100%, however although it actually released 105Ah charge.

Therefore for DOD, we prefer to using Ah instead of %.

SOC Estimation

OCV method

Voltage useful as indirect indicator of SOC, but not as measurement of SOC

Coulomb Counting

SOC (t) = SOC(0) -
$$\frac{1}{Q} \eta \int_0^t I(t) dt$$

η is cell coulombic efficiencyQ is the cell total capacity in ampere seconds(coulombs)

Cons: Accumulating error could be severe

State of Health

State of health estimation of cycle aged large format lithium-ion cells based on partial charging, Journal of Energy Storage, Volume 46, February 2022.

End of Life

- Battery Life requirements need to follow vehicle component requirements:
- 10 years and 150,000 miles.
- USABC has set requirements, based on both cycle life and calendar life.
- A battery is considered at its end of life if it cannot provide at least 80% of its initial capacity/energy, or 70% of its initial power (~130% of its original resistance).

Battery Degradation

Battery Degradation Scientifically Explained - EV Battery Tech Explained (https://www.youtube.com/watch?v=XLnBg25JoHg)

Battery Degradation

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State of Health

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State of Health

Review—"Knees" in Lithium-Ion Battery Aging Trajectories, Peter M. Attia *et al* 2022 *J. Electrochem. Soc.* **169** 060517

Key Impact Factors

Charging rate	High charging current expedites Li plating;
Discharging rate	Mixed
Voltage limit	Wide voltage window accelerates the onset of the knee point
Temperature	Studies found 25~35°C is the best
Rest time	Mixed
Pressure	Optimized in the intermediate value

Review—"Knees" in Lithium-Ion Battery Aging Trajectories, Peter M. Attia *et al* 2022 *J. Electrochem. Soc.* **169** 060517

Grand Challenges

- 1. Can we extend battery life by >3 times (cycle, calendar)?
- 2. How fast can batteries be charged (<10min)?
- 3. Can we make batteries be completely safe?
- 4. How do we sense the battery health condition?
- 5. How do we make battery wearable, flexible and stretchable?
- 6. How high energy density can batteries go (Wh/kg, Wh/L)?
- 7. Can we reduce the battery cost down by 3 times?
- 8. What are the methods for battery reuse and recycle?
- 9. How do we do grid-scale and seasonal storage?

Yi Cui, Stanford University

Li-ion Battery Present Development

Li-ion vs Na-ion

Important Parameters

- High energy capacity
- High power capacity
- High cyclability
- High safety

Large-scale ESS

Important Parameters

- Very long calendar life
- Very low cost
- High columbic efficiency

FARADION: Na-ion battery powered vehicle

Na-ion Battery

Why beyond Li-ion battery?

- Limited resources of lithium raw materials
- > Unevenly distributed (mainly in South America)
- Increasing demand

Why Na-ion battery?

- > Unlimited resources
- Physical and chemical similarity

	Li+	Na+
relative atomic mass (g/mol)	6.94	23
Shannon's Ionic radii (Å)	0.76	1.02
E ⁰ (vs SHE, V)	-3.04	-2.71
material abundance (ppm)	20	23,600
molar volume (\dot{A}^3)	21.3	39.3
theoretical capacity of ACoO ₂ /mAh g ⁻¹	274	235
theoretical capacity of ACoO ₂ /mAh cm ⁻³	1387	1193

N. Yabuuchi, et al., Chemical Reviews, 2014,114, 11636

Second-life Battery

Mitchell T. Smith, Michael R. Starke, Madhu Chinthavali, and Leon M. Tolbert, "Architecture for Utility-Scale Multi-Chemistry Battery Energy Storage", ECCE 2019.

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Battery Conventions

Т	ime	SOH
С	-rate	EOL
С	OCV	Capacity knee point
С	apacity	Resistance elbow
S	OC	
D	OD	
Ε	nergy	
Ρ	ower	
С	ycle number	
Ε	quivalent full cycles (or capacity/energy throughput)	
С	alendar life	
С	ycling life	
S	elf discharging current	

Conclusion

1. Battery electrochemical equations determine charge & energy density;

2. Solid-state &Na-ion battery deserve attentions in the near future;

3. Battery SOH has many unknowns, due to not enough data available;

4. In EECS domain, BMS, SOH and SLB are still important topics.

