Basics of Materials Selection for Lithium Ion Batteries as Advanced Energy Storage Devices

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Introduction

Batteries definition:

Two or more electrochemical cells, electrically interconnected, each of which contains two electrodes and an electrolyte. The redox (oxidation-reduction) reactions that occur at these electrodes convert electrochemical energy into electrical energy.

In everyday usage, 'battery' is also used to refer to a single cell. The solid-state batteries are the batteries in which the electrolyte is in solid state, which is responsible for the conduction of ions from one electrode to other electrode.

In 1800, Alessandro Volta invented the first modern battery.

Battery Types

Advantages and Limitations of Lead Acid Batteries

Advantages	Inexpensive and simple to manufacture — in terms of cost per watt hours, the SLA is the least expensive. Mature, reliable and well-understood technology — when used correctly, the SLA is durable and provides dependable service. Low self-discharge —the self-discharge rate is among the lowest in rechargeable batterysystems. Low maintenance requirements — no memory; no electrolyte to fill. Capable of high discharge rates.
Limitations	Cannot be stored in a discharged condition. Low energy density — poor weight-to-energy density limits use to stationary and wheeled applications. Allows only a limited number of full discharge cycles — well suited for standby applications that require only occasional deep discharges. Environmentally unfriendly — the electrolyte and the lead content can cause environmental damage. Transportation restrictions on flooded lead acid — there are environmental concerns regarding spillage in case of an accident. Thermal runaway can occur with improper charging.

Battery Types

Advantages and Limitations of NiMH Batteries

Advantages 30 – 40 percent higher capacity over a standard NiCd. The NiMH has potential for yet higher energy densities.
Periodic exercise cycles are required less often.
Simple storage and transportation — transportation conditions are not subject to regulatory control.
Environmentally friendly — contains only mild toxins; profitable for recycling.

Limitations Limited service life — if repeatedly deep cycled, especially at high load currents, the performance starts to deteriorate after 200 to 300 cycles. Shallow rather than deep discharge cycles are preferred.
Limited discharge current — although a NiMH battery is capable of delivering high discharge currents, repeated discharges with high load currents reduces the battery's cycle life. Best results are achieved with load currents of 0.2C to 0.5C (one-fifth to one-half of the rated capacity).
More complex charge algorithm needed — the NiMH generates more heat during charge and requires a longer charge time than the NiCd. The trickle charge is critical and must be controlled carefully.
High self-discharge — the NiMH has about 50 percent higher self-discharge compared to the NiCd. New chemical additives improve the self-discharge but at the expense of lower energy density.
Performance degrades if stored at elevated temperatures — the NiMH should be stored in a cool place and at a state-of-charge of about 40 percent.
High maintenance — battery requires regular full discharge to prevent crystalline formation.
About 20 percent more expensive than NiCd — NiMH batteries designed for high current draw are more expensive than the regular version.

Battery Types

Advantages and Limitations of NiCd Batteries

Advantages	Fast and simple charge — even after prolonged storage. High number of charge/discharge cycles — if properly maintained, the NiCd provides over 1000 charge/discharge cycles. Good load performance — the NiCd allows recharging at low temperatures. Long shelf life – in any state-of-charge. Simple storage and transportation — most airfreight companies accept the NiCd without special conditions. Good low temperature performance. Forgiving if abused — the NiCd is one of the most rugged rechargeable batteries. Economically priced — the NiCd is the lowest cost battery in terms of cost per cycle. Available in a wide range of sizes and performance options — most NiCd cells are cylindrical.
Limitations	Relatively low energy density — compared with newer systems. Environmentally unfriendly — the NiCd contains toxic metals. Some countries are limiting the use of the NiCd battery. Has relatively high self-discharge — needs recharging after storage.

Battery Types

Nickel Cadmium (NiCd) — mature and well understood but relatively low in energy density. The NiCd is used where long life, high discharge rate and economical price are important. Main applications are two-way radios, biomedical equipment, professional video cameras and power tools. The NiCd contains toxic metals and is environmentally unfriendly.

Nickel-Metal Hydride (NiMH) — has a higher energy density compared to the NiCd at the expense of reduced cycle life. NiMH contains no toxic metals. Applications include mobile phones and laptop computers.

Lead Acid — most economical for larger power applications where weight is of little concern. The lead acid battery is the preferred choice for hospital equipment, wheelchairs, emergency lighting and UPS systems.

Lithium Ion (Li-ion) — fastest growing battery system. Li-ion is used where high-energy density and lightweight is of prime importance. The technology is fragile and a protection circuit is required to assure safety. Applications include notebook computers and cellular phones.

Lithium Ion Polymer (Li-ion polymer) — offers the attributes of the Li-ion in ultra-slim geometry and simplified packaging. Main applications are mobile phones.

Lithium battery

There are two types of lithium-based batteries available.

1. Lithium batteries
2. Lithium-ion batteries

- In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable.
- In lithium-ion batteries, lithium compounds are used as anode.
- These batteries are known as re-chargeable batteries. Therefore, Lithium ion batteries are considered as best than pure Lithium based batteries.

Lithium battery

- Lithium is the lightest of metals and it can float on water.
- The electrochemical properties of lithium are excellent and it is also a highly reactive material.
- These properties gives Lithium the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power.
- Lithium batteries are primary batteries in which lithiun metal (or) lithium compound acts as a Anode. A lithuim cell can produce voltage from 1.5 V to about 3 V based on the types of materials used.

Types of batteries

Secondary batteries

In secondary batteries, the electrochemical reaction is reversible and the original chemical compounds can be reconstituted by the application of an electrical potential between the electrodes injecting energy into the cell.

Such cells can be discharged and recharged many times.

Types of batteries

Basically batteries can be classifieds as two types as primary batteries and secondary batteries.

Primary batteries

In primary batteries, the electrochemical reaction is not reversible.

During discharging the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted.

Thus the cells can be used only once.

Major Types of Materials

- Layered oxides
- Oxides with a spinel structure
- Poly-anion oxides with the olivine and olivine-related structures

Applications of Li-Ion Batteries

- The Li-ion batteries are used in cameras, calculators
- They are used in cardiac pacemakers and other implantable device
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers
- They are used to operate laptop computers and mobile phones and aerospace application

Li ion Battery components

Cathode materials	Old technology: $LiCoO_2$ $LiMn_2O_4$ $LiNiO_2$ New technology : LiFePO4	Store Li^+ ions and electrons in discharge mode
Electrolyte materials	Liquid solvent , gel, polymer And $LiPF_6$ or $LiClO_4$ Solid : **LiPON** , **γ-Li_3PO_4**	Transport Li^+ ions Exclude electrons
Anode materials	Li Al alloy Li intercalated graphite **Metal Li**	provide source of Li+ ions Make stable interface and electrons in discharge mode.

Construction of Lithium battery

- The electrolytes are selected in such a way that there should be an effective transport of Li-ion to the cathode during discharge.

- The type of conductivity of electrolyte is ionic in nature rather than electronic.

Construction Lithium battery

Li-ion cell has a four-layer structure.

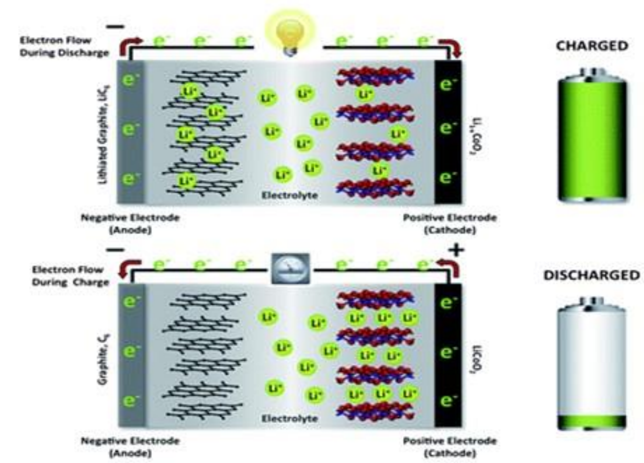
- A positive electrode made with Lithium Cobalt Oxide has a current collector made of thin aluminum foil - **cathode**

- A negative electrode made with specialty carbon has a current collector of thin copper foil
- A **separator** is a fine porous polymer film.
- An **electrolyte** made with lithium salt in an organic solvent.

Principle of Lithium battery

- During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery.
- Simply, the Li-ion is transfers between anode and cathode through lithium Electrolyte.
- Since neither the anode nor the cathode materials essentially change, the operation is safer than that of a Lithium metal battery.

How Lithium-Ion Batteries Work



Comparison of Battery Types

	NiCd	NiMH	Lead Acid	Li-ion	Li-ion polymer	Reusable Alkaline
Gravimetric Energy Density(Wh/kg)	45-80	60-120	30-50	110-160	100-130	80 (initial)
Internal Resistance (includes peripheral circuits) in mΩ	100 to 200[1] 6V pack	200 to 300[1] 6V pack	<100[1] 12V pack	150 to 250[1] 7.2V pack	200 to 300[1] 7.2V pack	200 to 2000[1] 6V pack
Cycle Life (to 80% of initial capacity)	1500[2]	300 to 500[2,3]	200 to 300[2]	500 to 1000[3]	300 to 500	50[3] (to 50%)
Fast Charge Time	1h typical	2-4h	8-16h	2-4h	2-4h	2-3h
Overcharge Tolerance	moderate	low	high	very low	low	moderate
Self-discharge / Month (room temperature)	20%[4]	30%[4]	5%	10%[5]	~10%[5]	0.3%
Cell Voltage(nominal)	1.25V[6]	1.25V[6]	2V	3.6V	3.6V	1.5V
Load Current - peak - best result	20C 1C	5C 0.5C or lower	5C[7] 0.2C	>2C 1C or lower	>2C 1C or lower	0.5C 0.2C or lower
Operating Temperature(discharge only)	-40 to 60°C	-20 to 60°C	-20 to 60°C	-20 to 60°C	0 to 60°C	0 to 65°C
Maintenance Requirement	30 to 60 days	60 to 90 days	3 to 6 months[9]	not req.	not req.	not req.
Typical Battery Cost (US$, reference only)	$50 (7.2V)	$60 (7.2V)	$25 (6V)	$100 (7.2V)	$100 (7.2V)	$5 (9V)
Cost per Cycle(US$)[11]	$0.04	$0.12	$0.10	$0.14	$0.29	$0.10-0.50
Commercial use since	1950	1990	1970	1991	1999	1992

Battery Types

Advantages and Limitations of Li-ion Polymer Batteries

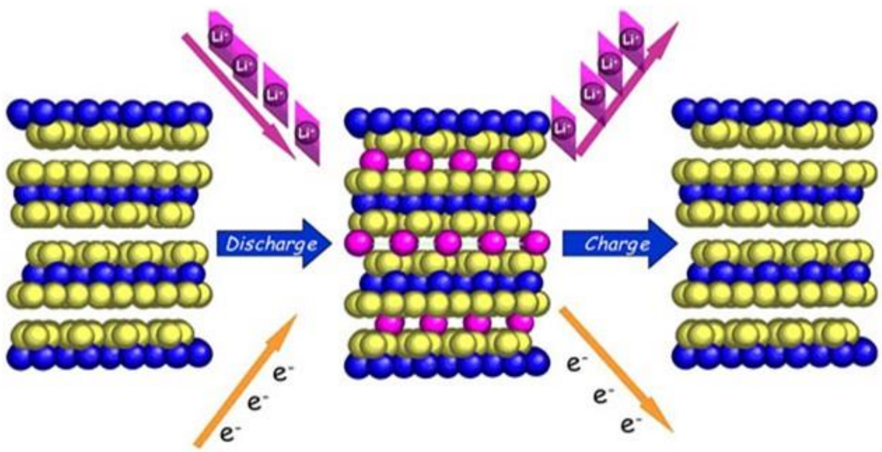
Advantages	Very low profile — batteries that resemble the profile of a credit card are feasible. Flexible form factor — manufacturers are not bound by standard cell formats. With high volume, any reasonable size can be produced economically. Light weight – gelled rather than liquid electrolytes enable simplified packaging, in some cases eliminating the metal shell. Improved safety — more resistant to overcharge; less chance for electrolyte leakage.
Limitations	Lower energy density and decreased cycle count compared to Li-ion — potential for improvements exist. Expensive to manufacture — once mass-produced, the Li-ion polymer has the potential for lower cost. Reduced control circuit offsets higher manufacturing costs.

Battery Types

Advantages and Limitations of Li-ion Batteries

Advantages	High energy density — potential for yet higher capacities. Relatively low self-discharge — self-discharge is less than half that of NiCd and NiMH. Low Maintenance — no periodic discharge is needed; no memory.
Limitations	Requires protection circuit — protection circuit limits voltage and current. Battery is safe if not provoked. Subject to aging, even if not in use — storing the battery in a cool place and at 40 percent state-of-charge reduces the aging effect. Moderate discharge current. Subject to transportation regulations — shipment of larger quantities of Li-ion batteries may be subject to regulatory control. This restriction does not apply to personal carry-on batteries. Expensive to manufacture — about 40 percent higher in cost than NiCd. Better manufacturing techniques and replacement of rare metals with lower cost alternatives will likely reduce the price.

Layered oxides



Octahedral <LiO_6> arrangement allows ion movement from one (vacant) octahedral-site plane to another via a tetrahedral site.

Cathode Materials

Material category	Structure	Synthetic method	Voltage range	Capacity (mAh g^{-1})
$LiMO_2$	Layered structure	Co-precipitation, sol-gel, hydrothermal method, solid-state reaction, etc.	2.8–4.3 V	~200
Li-rich oxides	Layered structure	Co-precipitation, sol-gel, hydrothermal method, solid-state reaction, etc.	2–4.8 V	>250
V_2O_5	Layered structure	sol-gel, hydrothermal method, solid-state reaction, etc.	2.0–4.0 V	~270
V_6O_{13}	Layered structure	sol-gel, hydrothermal method, solid-state reaction, etc.	2.0–3.4 V	~290
VO_2	Layered structure	sol-gel, hydrothermal method, solid-state reac-tion, etc.	1.0–4.0 V	~300
LiV_3O_8	Layered structure	sol-gel, hydrothermal method, solid-state reac-tion, etc.	2.0–4.0 V	~310
$LiNi_{0.5}Mn_{1.5}O_4$	Spinel	Solid-state reaction, mol-ten salt, sol-gel, co-precipitation, etc.	3.5–5 V	~130

Cathode Materials

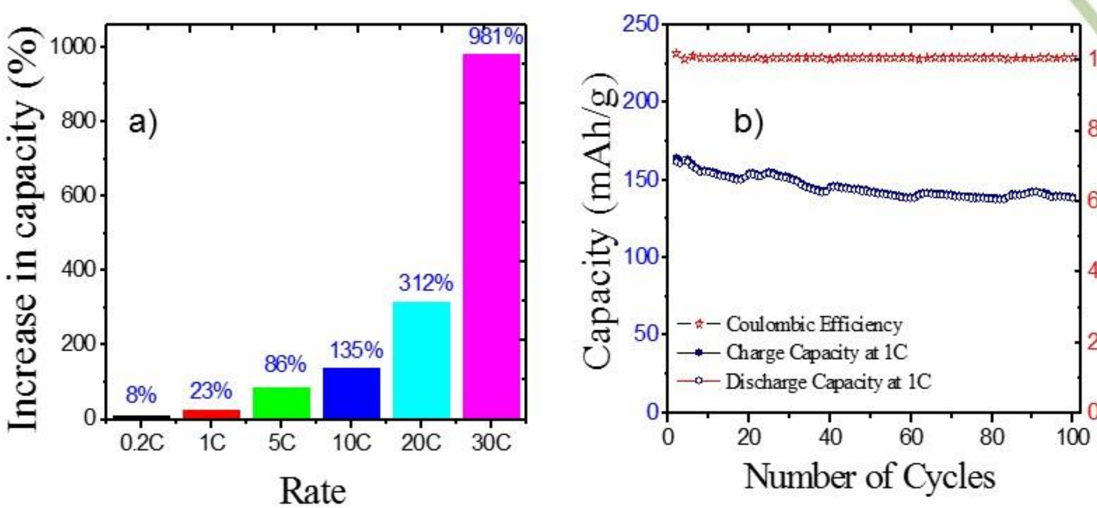
Electrochemical characteristics of the three classes of insertion compounds.

Framework	Compound	Specific capacity [a] (mAh g^{-1})	Average potential (V *vs.* Li^0/Li^+)
Layered	$LiCoO_2$	272 (140)	4.2
	$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$	272 (200)	4.0
Spinel	$LiMn_2O_4$	148 (120)	4.1
	$LiMn_{3/2}Ni_{1/2}O_4$	148 (120)	4.7
Olivine	$LiFePO_4$	170 (160)	3.45
	$LiFe_{1/2}Mn_{1/2}PO_4$	170 (160)	3.4/4.1

Comparison of current commercialized cathode materials

Material category	$LiCoO_2$	$LiNiO_2$	$LiFePO_4$	$LiMn_2O_4$
Cost (kWh)	High	Average	Low	Low
Safety	Average	Poor	Good	Average
Cyclic life	Average	Poor	Good	Poor
Energy (Wh kg^{-1})	Good	Good	Poor	Average

Zn Doped Mesoporous TiO_2 Microspheres



(a) Percentage increase in discharge capacity of Zn doped mesoporous TiO_2 and 20 nm anatase TiO_2 nanoparticles at different discharge rates. (b) Cycling performance and Columbic efficiency of Zn doped mesoporous TiO_2 up to 100 cycles at 1C charge/discharge rates.

Anode Materials Requirements

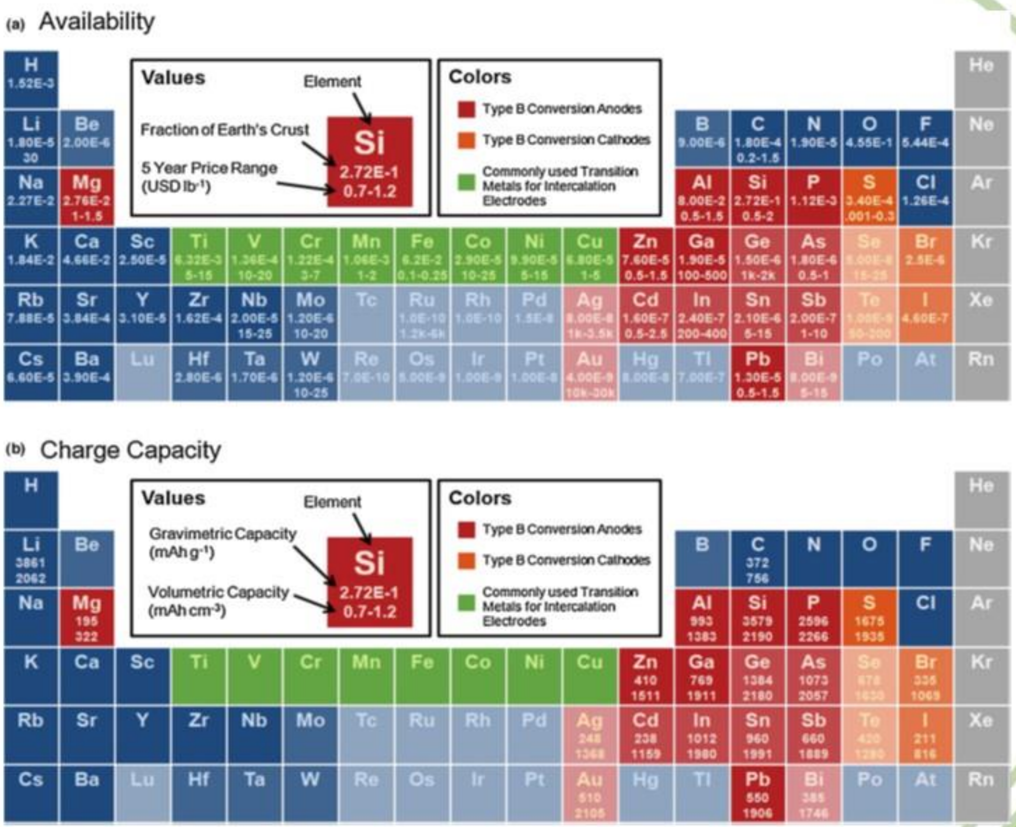
- Large reversible capacity
- Small irreversible capacity
- Desirable charge profile
- Desirable kinetics (rate capability)
- Long cycle and calendar life
- Ease of processing
- Safety
- Compatibility with electrolyte and binder systems
- Low cost

Anode Materials

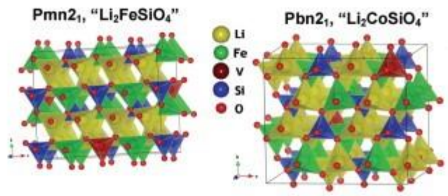
Most common anode materials used for lithium ion batteries.

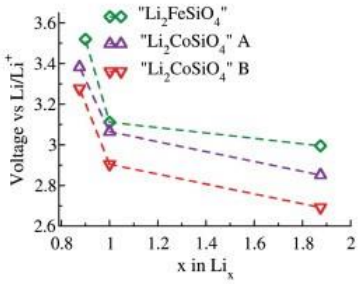
Active anode material	Theoretical capacity ($mAh\ g^{-1}$) [Reference]	Advantages	Common issues
Insertion/de-insertion materials			
A. Carbonaceous a. Hard carbons b. CNTS c. Graphene	200-600 1116 780/1116	➢ Good working potential ➢ Low cost ➢ Good safety	❖ Low coulombic efficiency ❖ High voltage hysteresis ❖ High irreversible capacity
B. Titanium oxides a. $LiTi_4O_5$ b. TiO_2	175 330	➢ Extreme safety ➢ Good cycle life ➢ Low cost ➢ High power capability	❖ Very low capacity ❖ Low energy density
Alloy/de-alloy materials			
a. Silicon b. Germanium c. Tin d. Antimony e. Tin oxide f. SiO	4212 1624 993 660 790 1600	➢ Higher specific capacities ➢ High energy density ➢ Good safety	❖ Large irreversible capacity ❖ Huge capacity fading ❖ Poor cycling
Conversion materials			
a. Metal oxides(Fe_2O_3, Fe_3O_4, CoO , Co_3O_4, Mn_xO_y, Cu_2O/CuO, NiO, Cr_2O_3, RuO_2, MoO_2/MoO_3 etc.)	500–1200	➢ High capacity ➢ High energy ➢ Low cost ➢ Environmentally compatibility	❖ Low coulombic efficiency ❖ Unstable SEI formation ❖ Large potential hysteresis ❖ Poor cycle life
b. Metal phoshides/sulfides/nitrides (MXy; M = Fe, Mn, Ni, Cu, Co etc. and X = P, S, N)	500–1800	➢ High specific capacity ➢ Low operation potential and Low polarization than counter oxides	❖ Poor capacity retention ❖ Short cycle life ❖ High cost of production

Materials Selections for Batteries



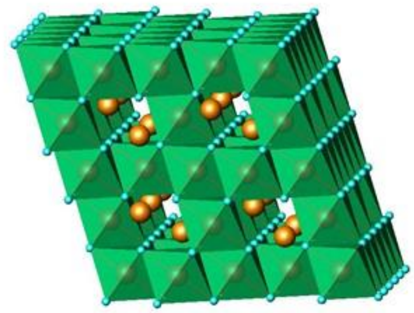
Poly-Anion Compounds





Materials with open 3D frameworks, which are available for Li migration

Spinel Structures



Tetrahedral sites provide 3D paths for Li^+ diffusion through the spinel framework

Thank you for your attention!