Manufacturing and recycling of Li-ion cells

ATHENS WUT21 course

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Functional additives for electrolytes

- Conductivity enhancing additives;
- Absorbent additives (or gas formation inhibitors):
  - for gaseous products of SEI formation and solvent decomposition (CO_2, H_2, hydrocarbons);
  - for products of $LiPF_6$ decomposition (HF);
  - water scavengers.
- Additives enhancing thermal and chemical stability of $LiPF_6$;

Functional additives for electrolytes

- Additives protecting against overcharge:
  - redox shuttles, oxidize and regain their original form at the cathode;
  - insulates anode through polymeric protective layer formation or through gas formation in case of overcharging;
- Additives enhancing separator wettability, decreasing viscosity;
- Additives increasing ionic dissociation:
  - increases lithium salt solubility;
  - anion receptors;

Functional additives for electrolytes

- Additives that affect lithium reduction on electrodes:
  - dendrites removal;
  - surfactants;
  - form alloys with lithium;
- Additives that inhibit aluminum corrosion;
- Flame retardant additives:
  - free radical acceptors that make ignition more difficult;
  - solvents that cannot ignite.

Functional additives for electrolytes

- Additives enhancing SEI layer:
  - stabilizing decomposition products;
  - building into the electrode surface;
  - weakening lithium solvation by carbonates / weaker co-intercalation;
  - dissolving LiF crystals;
  - weakening reductive properties of graphite;
  - polymerizing to tighten SEI layer;
  - reducing instead of carbonates and thus polymerizing.

Functional additives for electrolytes

- Additives are used usually up to 25% of total content. The most common additives are FEC, VC, TMP or other phosphines, less common are LiF, Li_2CO_3, LiTDI and LiBOB. The highest concentrations (10%) are used in case of FEC and TMP, others are used usually up to 5%;
- It is important to remember, that every additive even in smallest amount is not only changing properties connected with its function, but can also change all other properties of the electrolyte (conductivity, lithium cation transference number) or even whole cell (SEI equilibria, for instance).

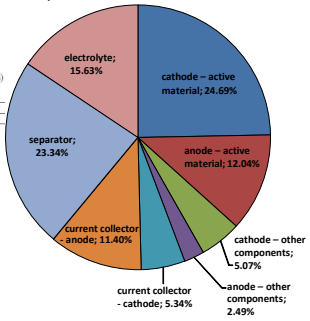
Non-active cell components

Non-active cell components comprise ca. 33-40% of cost and 33% of cell's mass (without case, which for cylindrical – steel can – is another 25-30% of the cell's inner mass)

Table A-1. Cost of Materials in Cell Windings of a 40-kW 48-Cell Battery (24.7-Ah cells) That Employs the Gen 2 Cell Materials

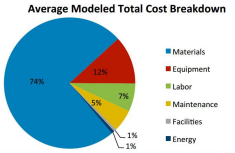
Type of Material	40-kW Maximum Power-Assist Battery Quantity	Unit Cost	Cost, $
Cathode			
Active material ($LiNi_{0.4}Co_{0.15}Al_{0.05}O_2$)	7.707 kg	20.52/kg	158.15
SFG-6	0.367 kg	15.00/kg	5.51
Carbon black	0.367 kg	6.82/kg	2.50
PVDF binder	0.734 kg	10.00/kg	7.34
NMP binder solvent	5.383 kg	3.18/kg	17.12
Anode			
Active material	5.143 kg	15.00/kg	77.15
PVDF binder	0.478 kg	10.00/kg	4.78
NMP binder solvent	3.504 kg	3.18/kg	11.14
Aluminum foil current collector	34.18 m^2	1.00/m^2	34.18
Copper foil current collector	36.53 m^2	2.00/m^2	73.07
Separator	74.77 m^2	2.00/m^2	149.54
Electrolyte ($LiPF_6$ in EC:EMC)	5.01 liters	20.00/L	100.14
Total material cost			640.61

G.L. Henriksen, K. Amine, J. Liu, P.A. Nelson, ANL-03/5

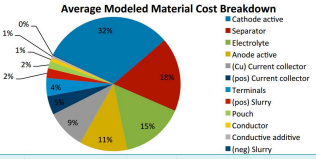


Non-active cell components

Average Modeled Total Cost Breakdown



Average Modeled Material Cost Breakdown



Part	Description	unit	U.S. Startup U.S.-Based New Entrant[4]	U.S. Transplant Korea Owned, U.S. Factory	Japan Japan Owned, Japan Factory	Korea Korea Owned, Korea Factory	Tier 1 China China Owned, China Factory	Tier 2 China China Owned, China Factory	Mexico Japan Owned, Mexico Factory
Anode active material	Natural graphite (carbon coated)	USD/ kg	$14.87	$14.87	$ 14.87	$13.09[1]	$13.09[1]	$13.09[1]	$ 14.87
	Synthetic graphite	USD/ kg	$18.00	$18.00	$18.00	$15.84[1]	$15.84[1]	$15.84[1]	$18.00
Binder	SBR (5.0 wgt-%)	USD/ kg	$6.00	$5.52[1]	$5.52[1]	$5.52[1]	$5.52[1]	$5.52[1]	$5.52[1]
Solvent	Water (96 wgt-% of slurry mix)	USD/ kg	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Current collector	12 um Rolled Copper	USD/ m^2	$1.80	$1.66[1]	$1.66[1]	$1.66[1]	$1.66[1]	$1.66[1]	$1.66[1]
Cathode active material	NMC333-G (89 wgt-%)	USD/ kg	$30.00	$24.00[1]	$24.00[1]	$20.10[1]	$20.10[1]	$18.00[1]	$24.00[1]
Conductive materials	Carbon black (6 wgt-%)	USD/ kg	$7.50	$6.90[1]	$6.90[1]	$6.90[1]	$6.90[1]	$6.90[1]	$6.90[1]
Binder	PVDF (5 wgt-%)	USD/ kg	$30.00	$27.60[1]	$27.60[1]	$27.60[1]	$27.60[1]	$27.60[1]	$27.60[1]
Solvent	NMP (96 wgt-% of slurry mix)	USD/ kg	$18.00	$16.56[1]	$16.56[1]	$14.40[1,2]	$14.40[1,2]	$14.40[1,2]	$16.56[1]
Current collector	20 um Aluminum	USD/ m^2	$0.80	$0.74[1]	$0.74[1]	$0.74[1]	$0.74[1]	$0.74[1]	$0.74[1]
Separator	20 um PP (uncoated)	USD/ m^2	$2.00	$1.84[1]	$1.84[1]	$1.84[1]	$1.84[1]	$1.84[1]	$1.84[1]
	20 um PVDF based	USD/ m^2	$5.00	$4.60[1]	$4.60[1]	$4.60[1]	$4.60[1]	$4.60[1]	$4.60[1]
Electrolyte	EC/DMC/MEC-LiPF6	USD/ kg	$19.57	$18.00[1]	$18.00[1]	$18.00[1]	$18.00[1]	$18.00[1]	$18.00[1]

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Separators

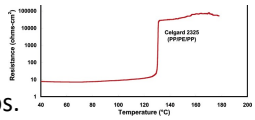
Main purposes of the separator is:

- Physical separation of electrodes (prevention against short circuit);
- Electric insulation (no electronic conductivity);
- Enabling electrolyte flow;
- Enhancing contact with electrode surfaces (wetting them with electrolyte) even at increased temperature or after the bending (rolling sheets to cylindrical shape);
- Other functions (*e.g.* protection against overheating).

Separators

Required separators properties:

- Good wettability and absorbability (quick and full);
- Good electronic insulator;
- High porosity (40-60%, pores <1 μm diameter);
- Compatibility with other cell components;
- Resistance to high or low potentials;
- Thermal stability and no measurable shrinkage or crimping at elevated temperature (up to 90°C);
- Closing pores in case of really high temperature (>130°C);
- Resistant to compression;
- No impurities, holes and crimps.



Separators

Separator should not influence any other cell parameters (including resistance), aside from safety aspects – those should be increased.

Separator usually keeps electrolyte with capillary forces, thus, it should have good contact with electrodes; otherwise, in places where separator is not tightly pressed onto electrode, electrolyte can lose contact with electrode.

Separators have to prevent whiskers from growing through them, as well as prevent puncture by any other crystallites formed at the electrodes surfaces; otherwise, short circuit may occur.

Separators

Separator is usually a non-woven fabric or porous membrane made of PE, PP, other polymers, copolymers, multilayer fibers or fibers doped with ceramic materials (or flame retardants). There are also separators made of porous ceramics or formed *in situ* from flexible porous materials (thus maintaining good contact with electrodes). Separators made from glass fiber (woven) or kevlar (polyaramides) also exist.

Separators can be 10-200 μm thick, although usually they have thickness in 10-30 μm range (depending on application). However, even very thin ones can decrease electrolyte conductivity few-fold (up to six-fold).

Current collectors

Current collectors purpose is to lead in and off electrons produced/consumed by electrode reactions. Their purpose is good electron conductivity, resistance to harsh conditions inside the cell (temperature, chemicals, oxidation, reduction) and good contact with electrode active material.

Current collectors

Current collectors should be as thin as possible, but thick enough to withstand mechanical stresses, bending (during cell manufacturing), as well as pressure during cell operation. All of these have to be endured even after weakening by corrosion due to contact with hydrogen fluoride (HF) and other oxidative or reductive chemicals at high temperatures (up to 80°C) and alternating potential.
In commercial cells, copper (anode) and aluminum (cathode) foils have 5-15 µm thickness. Aluminum is lighter (3x lower density) and much cheaper, but forms alloys with lithium at low potentials, so it cannot be used for anodic current collector.

Binders

Binder is used to stick together active material (AM), which usually has a form of powder, and form uniform mass with homogeneous distribution of AM. At the same time the objective is to distribute AM particles in material in such a way that it had good contact and homogeneous distribution of functional additives and conductive additives around them (in case of cathodes and non-carbon anodes). Common features of binders are: preventing agglomeration of electrode components grains, formation of uniform layer tightly fitting to AM grains and maintaining ionic and electronic conductivity.

Binders

Too low amount of binder does not enable good conductivity yet. Too high amount decrease active mass content and weakens its contact with conductivity enhancing additives. The thickness of the poorly conducting binder layer also becomes too big.

The most common binder is PVdF (poly(difluorovinylidene), latex), however lately also modified cellulose starts to take it share, as well as PVP (poly(vinylpyrrolidone)) and nonfluorinated rubbers. Binder content can be used in the 2-20% range, depending on the design and requirements, but most commonly is now used in 2-5% range.

Conductivity enhancing additives

Conductivity enhancing additives work according to their name ☺ (it is electronic conductivity). Anodes based on carbon materials such as graphite, carbon black, hard carbon, soft carbon or carbon nanotubes conduct well on their own, thus, they do not need such additives. On the other hand all cathode materials and non-carbon anode materials conduct poorly or very poorly, so they do need such additives.

Conductivity enhancing additives

Additives for conductivity enhancement are usually carbon materials, such as carbon black, acetylene black, graphite and sometimes other forms of carbon. Particularly acetylene black has a tendency to form agglomerates which are branched. It is a positive thing, as it allows to use very small amount of acetylene black while keeping percolation threshold very low. Additives content are usually in the 2-15% range, however their total content should not exceed binder content in the electrode final mass.

Casings

Traditionally casing was made of thin steel or stainless steel plate. Nowadays, casings made of plastics are more common (*e.g.* PE, PP), which are lighter and at least as resistant as steel (usually more resistant) against the chemicals present in Li-ion cell. In prismatic cells special foils (so-called coffee bags) are usually used for casing – they are made of aluminum foil laminated on both sides (*e.g.* with PE and PET) in order to enhance its mechanical properties (resistance to stretching, for instance). Molded plastic forms are also used and are thermally bonded.

Passive layer/interphase

It is not a component that can be added; It is formed (mostly at anode surface) during cell manufacturing process and then during operation of a cell (it starts to form in the moment of first contact between components with each other). It consists of both organic and inorganic compounds.

Passive layer/interphase

Solid-Electrolyte Interphase (SEI) objective is to protect anode/cathode/lithium from further reaction with the electrolyte and its impurities or products of the previous side reactions.

SEI has to conduct ions well and be selective for Li cations. It means that SEI should easily pass Li^+, but it should not let through anions, solvent molecules or additives.

In order to ensure good overall conductivity, it should be as thin as possible.

Passive layer/interphase

The most important thing is that passive layer should be as thin as possible and so it should not grow over time. Only then small amounts of salt, solvent and electrode material are consumed on SEI formation. SEI formation is responsible for resistance increase in electrolyte and/or active mass content decrease in electrodes which results in cell capacity drop.

High inorganic compounds content in SEI favors thin, stable and selective SEI. High organic compounds content in SEI means decrease of selectivity and its poorer stability over time.

Adequate choice of electrolyte additives use, composition of electrodes and electrolyte allow to engineer (to a certain degree) both composition and thickness of SEI.

Chemical protection means

Chemical protection methods include: functional additives to electrodes and electrolyte that block electrode reactions above certain temperature or above certain potential (through polymerization, catching free electrons). Overcharging and/or too high current can also initiate reaction of additives blocking the given oxidation/reduction potential or the whole cell.

Mechanical protection means

Mechanical protection methods include various separators, which above certain temperature start to flow (pores close, porosity decrease). Thanks to that resistance increases by several orders of magnitude which leads to blocking all cell processes.

Apart from that, some binders and electrode additives can provide similar reaction to temperature.

Electronic protection means

Battery Management System (BMS) usually cooperates with sensors inside the modules, battery packs or individual cells.
Upon detection of too high current, voltage or temperature, too low resistance or too sudden changes of those parameters (depending on the exact nature of sensors and algorithm) BMS can be designed in such a way that it can stop the charge or discharge of the cell/module/pack or start to equalize/buffer current between cells/modules.

On cell sizes

Cylindrical and button (coin) cells are standardized in their size notation. Their designations are their dimensions.

First two digits (usually) are their diameter in millimeters and all the other digits are length/height in tenths of a millimeter (within the tolerances). These are the external dimensions of the whole cell including the casing.

On cell sizes

For instance:

- 2032 (the most popular coin cell) have 20 mm diameter and 3.2 mm height;
- 18650 (until recently the most common cylindrical cell for notebooks, also used in Tesla cars; high power – for applications that require high current – have up to 2500 mAh, but capability for fast charge/discharge e.g. 5-10C; high energy – optimized for high capacity – have up to 3600 mAh, but work poorly or have low capacity when subject to high currents, above 1C) have 18 mm diameter and 6.5 cm height (65.0 mm);
- 20700 i 21700 – (introduced in 2018 by Tesla, Panasonic, LG and Samsung; have ca. 1.3 times higher capacity compared to 18650, but are harder to manufacture and to cool down) have 20 mm diameter and 70 mm height; often designated wrong by manufacturers themselves – as 2070 i 2170.

Recycling

Most of cells, at least those bigger (*e.g.* for EV or HEV) can be used again after removing them from the car, as it still has 70-80% of the nominal (initial) capacity. It is more then suffice for power grid frequency/voltage regulation or as a backup power. Second use of the cell is making its use and price more economic (thanks to buy back system after consumer finishes using it).

Recycling

Until recently the only method implemented on big scale (called pyrometallurgical) consists in putting all components to a big furnace and burn it at temperatures above 2000°C. It is not possible to recover the most expensive components that way (in terms of price of the highly processed components, like separator or electrolyte). However, it enables recovery of raw materials used initially for cell manufacturing, like metals in a very pure form, as from the basic raw materials costs point of view they are the most expensive ones.

Recycling

Pyrometallurgical method consists in thermal decomposition of the whole processed batch (cells along with casings). Due to the high temperature, all polymers and other organic materials after evaporation to carbon dioxide and water vapor are removed. Chlorine, fluorine and even part of carbon and phosphorous (originating from the electrolyte and/or additives) are also evaporated in form of compounds or pure gases (toxic ones are caught on filters).

Recycling

At the bottom of the furnace remain only metals in the liquid form which separate to layers according to density differences. Thus, metals can be poured in fractions of relatively pure metals or their alloys. Only metals unprofitable to recycle (such as aluminum or iron), contaminated graphite and silicon are disposed.

Hydrometallurgical method

For few years now new method is gaining popularity: first the separation (after crushing) of copper, aluminum, plastics (separator, casing) and steel (if present) from the electrode materials takes place. Subsequently electrode materials are leached with acids and basics to get metals in salt form (e.g. sulfates) and then with metallurgical and/or electrochemical methods separate metals from each other. The advantage of the method is few times smaller furnace charge (energy and money savings) and the recycling rate of most metals is much higher (and they are purer). Method is more and more often used (in different variants).

Recycling technologies comparison

Table 2. Summary of LiB recycling processes.

Process	Feed	Pre-Processing	Mechanical Processing	Pyro	Hydro	Main Recoveries	Secondary Recoveries	Use of Main Recoveries	Use of Secondary Recoveries	Losses
Umicore ValEas™	LIB, NiMH	Dismantling	-	Shaft furnace	Leaching solvent extraction	Co, Ni, Cu, Fe $CoCl_2$	Slag: Al, Si, Ca, Fe, Li, Mn, REE	Metal industry, cathode production	Construction industry	Electrolyte, plastics, graphite
Sumitomo–Sony	LIB.	Sorting Dismantling	-	Calcination	Hydro	CoO	Co–Ni–Fe alloy Cu, Al, Fe	Battery industry	Metal industry	Electrolyte, plastics, Li, Ni, graphite
Retriev Technologies	LIB Primary Li	Dismantling	Wet comminution, screening, shaking table, filtration,		Precipitation	Li_2CO_3 MeO	Steel Cu, Co, Al	Cathode production, metal industry	Metal industry	Plastic
Recupyl Valibat	LIB Primary Li	-	crushing, vibrating screen, secondary screen, magnetic separator, densimetric table,	-	Hydrolysis leaching	Li_2CO_3, $LiCO_2$, Li_3PO_4	Steel Cu, Al Cu, MeO, C	Cathode Production.	Metal industry	Cu, graphite
Akkuser	LIB	Sorting	1st cutting, air filtration, cutting, magnetic separator	-	-	Co, Cu powder Fe	Non-ferrous metals	Various including metal industry	Metal industry	Plastic
Accurec	LIB	Sorting Dismantling	Milling, separation, agglomeration, filtration, ambient	Vacuum thermal treatment, reduction	H_2SO_4	Li_2CO_3 Co-Alloy	Metallic alloy	Production of cathode material	Metal recovery	Electrolyte, polymers, graphite
Battery Resources	LIB	Discharge	Shredding, magnetic separation, sieving, dense media; ambient	Sintering	Leaching by: NaOH, H_2O_2, H_2SO_4, and Na_2CO_3	Li_2CO_3 $NMC(OH)_2$	Ferrous metals	Battery cell production	Metal industry	Electrolyte
LithoRec	LIB	Discharge Manual disassembly	Two-stage crushing, two-stage air classification; inert.	Drying, calcination	Undisclosed leaching agent	Li_2CO_3 metal oxides	Al–Cu, plastic fractions	Battery cell production	Metal industry	Electrolyte
OnTo	LIB Primary Li	Discharge Dismantling	Shredding, sieving dense media separation; supercritical CO_2	Present (undisclosed).	Leaching purification, dissolution	Refurbished cell cathode powder	Ferrous and non-ferrous metals	Battery cell production	Metal industry	Binder, graphite
Aalto University	LIB	-	Shredding, sieving	Aluminium smelter	Leaching	CoC_2O_4 Al	Jarosite, manganese dioxide, copper hydroxide, Li–Ni solution.	Reprocessing required	Reprocessing required	Graphite, binder plastic, Cu, water

O. Velazquez-Martinez, J. Valio, A. Santasalo-Aarnio, M. Reuter, R. Serna-Guerrero, Batteries 5 (2019), 68.

Recycling technologies comparison

Cathode active material and lithium recovery rate

Table 3. Cathode material recovery summary of the recycling processes.

Process	Co Recovery	Quality of Recovery
Umicore	$CoCl_2$	Ready for $LiCoO_2$ synthesis
Sumitomo–Sony	CoO	Recovery needs pyrometallurgical processs before cathode synthesis
Retriev Technologies	MeO + cake	Elemental cobalt
Recupyl	$LCO/Co(OH)_2/Co$	final product
Akkuser	Co + graphite	Recovery requires hydro- and/or pyrometallurgical processes before cathode synthesis
Accurec	Co alloy	Elemental cobalt
Battery Resources	$NMC(OH)_2$	Ready for cathode synthesis
LithoRec	MeO	Ready for cathode synthesis
OnTo	Cathode powder (refurbished)	Final product
Aalto University	CoC_2O_4	Recovery requires processing

Table 4. Lithium recovery summary of the recycling processes.

Process	Li Product	Recovery Method	Efficiency	Recovery Quality	Target Use of Recovery
Umicore	Not recovered	-	-	-	-
Sumitomo–Sony	Not recovered	-	-	-	-
Retriev Technologies	Li_2CO_3	Precipitation with Na_2CO_3/CO_2	90%	No data	Metal manufacture
Recupyl	Li_2CO_3/Li_3PO_4	Precipitation with CO_2	No Data	No data	Not discussed
Akkuser	Not recovered	-	-	-	-
Accurec	Li_2CO_3	Precipitation	76–90%	>99%	Glass production/cathode synthesis
Battery Resources	Li_2CO_3	Precipitation with Na_2CO_3	67–80%	"High Purity"	Cathode powder synthesis
LithoRec	Li_2CO_3/LiOH	Precipitation	85–95%	No Data	Cathode powder synthesis
OnTo	Li_2CO_3/cathode	Undisclosed	Undisclosed	99%	Battery production
Aalto University	Li–Ni solution	Leaching	93–97%	0.1%	Not discussed

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Recycling technologies comparison

Non-cathode metals recovery rate

Table 5. Metal recovery summary of the recycling processes.

Process	Fe Casing	Al and Cu Foils	Losses
Umicore	Fe: recovered in alloy	Cu: recovered in alloy	Al, polymer
Sumitomo–Sony	Fe: recovered in alloy	Cu: recovered.in alloy	Al, polymer
Retriev Technologies	Fe, Al, and plastics: recovered in shaking table	Not mentioned.	Not mentioned
Recupyl	Fe: recovered with magnetic separator	Al, Cu, and plastics: recovered with density separation	Not mentioned
Akkuser	Fe: recovered with magnetic separator Plastics: recovered via air filtration	Al and Cu: recovered from fin powder	Fraction of Cu and Al
Accurec	Fe: recovered with magnetic separator	Al and Cu: recovered via air separator	Polymer
Battery Resources	Fe: recovered with magnetic separator	Al: recovered during leaching Cu: recovered via dense media separation and precipitation	Not mentioned
LithoRec	Fe, Al, and plastics: recovered via air separator	Al and Cu: recovered via sieves and zig-zag sifter	Not mentioned
OnTo	Fe, Al, and plastics: recovered	Al and Cu: recovered	Not mentioned
Aalto University	Fe: extracted at pre-processing	Rotary kiln	Cu, graphite.

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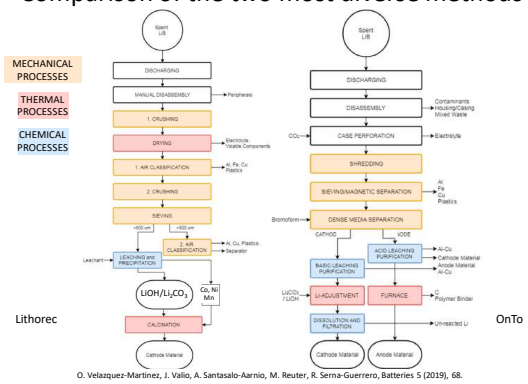
Recycling technologies comparison

Comparison of the two most diverse methods



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First charge and charging conditions

First charge is usually performed employing C/20 rate, as higher current does not enable proper intercalation and full filling of free sites in the anode volume.

First charge (and the next ones, if they are made in controlled environment/conditions) are performed using CC-CV method, which stand for 'constant current, constant voltage'. First charge is made using constant current until a predefined cut-off voltage is obtained, *e.g.* at 4.2 V. Then charge is continued with constant voltage but with decreasing current until current obtains defined lower limit (cut-off current, usually set as a current equal to C/50 rate).

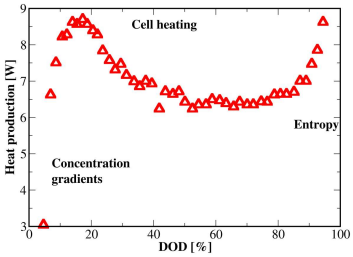
Coulombic efficiency vs overall efficiency

Coulombic efficiency (CE), which is most commonly used by electrode researchers, electrode testers and cell manufacturers, is a fraction of charge that is used on reactions that charge or discharge the cell. In Li-ion cells such efficiency usually exceeds 99% (apart from the first charge, in which SEI is forming, which consumes some energy), while in NiMH or NiCd it is usually much lower (~95%), as side reactions occur in them.

Coulombic efficiency vs overall efficiency

'Round trip efficiency' of the cell is in reality lower than it would result from CE only. Efficiency calculated from energy recovered from a cell (during discharge) divided by energy intake (during charge) includes heat losses, increasing overpotentials and losses on concentration gradient formation and on maintaining it. The last one has an impact particularly when high charge/discharge or pulse currents are used.

Heat losses



L.O. Valøen, M.I. Shoesmith, *The effect of PHEV and HEV duty cycles on battery and battery pack performance*, PHEV 2007.

Heat produced in a cell with 3 Ah capacity during 6.7C rate discharge (20 A). Concentration gradient formation range is visible as well as cathode filling range (entropy).