

Batteries

ACME Faculty, EHVE course
B.Sc. Studies, III year, V semester

Leszek Niedzicki, PhD, DSc, Eng.

Components for Li-ion cells and nonstandard electrolytes

Functional additives for electrolytes

- Conductivity enhancing additives: FEC, DME (dimethoxyethane), nano- and micro-particles of ceramic fillers like Al_2O_3 or TiO_2 (surface can be modified with acidic or basic groups);
- Absorbent additives (or gas formation inhibitors) for gaseous products of SEI formation and solvent decomposition or LiPF_6 decomposition; capturing CO_2 , HF, H_2O , etc. Those are aromatic isocyanates, alkyl amines, aminosilanes, imides.
- Additives enhancing thermal and chemical stability of LiPF_6 , e.g. LiF, TFEP, NMP. They capture free radicals of PF_5 .

2

Functional additives for electrolytes

- Additives protecting against overcharge, e.g.: difluoroanisole, anthracene, *p*-dimethoxybenzene derivatives, lithium fluorodecaborane (redox shuttles, oxidize and regain their original form at the cathode), diphenylalkanes, thiophene derivatives, LiBOB, xylene (insulates anode through polymeric protective layer formation or through gas formation in case of overcharging), etc.;
- Additives enhancing separator wettability (e.g. TMP, TEP, cyclohexane), decreasing viscosity (e.g. P_2O_5);
- Additives increasing ionic dissociation, for instance: 12-crown-4 ether (increases lithium salt solubility), alkylboranes, perfluoroarylborates (anion receptors);

3

Functional additives for electrolytes

- Additives that affect lithium reduction on electrodes, e.g.: nitromethane, SO_2 , polysulfides, FEC, 2-MeTHF (dendrites removal), alkylammonium chlorides, prefluoroalkylsulfonate salts, perfluoropolyethers, nitrocellulose (surfactants), AlI_3 , SnI_2 (form alloys with lithium);
- Additives that inhibit aluminum corrosion, e.g.: LiBOB, LiDFOB;
- Flame retardant additives, e.g.: TMP, TEP, HMPN (those are alkyl phosphines and cyclophosphazenes) (free radical acceptors that make ignition more difficult), methoxyperfluorobutane, fluorinated PC (solvents that cannot ignite);

4

Functional additives for electrolytes

- Additives enhancing SEI layer:
 - stabilizing decomposition products: Li_2CO_3 , maleic anhydride or NBS;
 - building into the electrode surface: B_2O_3 , trialkylborates, trialkoxyborates, LiBOB;
 - weakening lithium solvation by carbonates (weaker co-intercalation): NaClO_4 , K_2CO_3 ;
 - dissolving LiF crystals: tris(pentafluorophenyl)borate.

5

Functional additives for electrolytes

- Additives enhancing SEI layer cont'd:
 - Weakening reductive properties of graphite: SO_2 , CS_2 , polysulfides, arylsulfides, silanes, siloxanes, fluorinated compounds;
 - polymerizing to tighten SEI layer: alkyl nitrates, BrGBL, FEC;
 - reducing instead of carbonates and thus polymerizing: VC, siloxanes with vinyl group, vinyl esters, 2-vinylpyridine, acrylonitrile, 2-furonitrile, phosphonates.

6

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 and LiBOB. The highest concentrations (10%) are used in case of FEC and TMP, others are used 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).

7

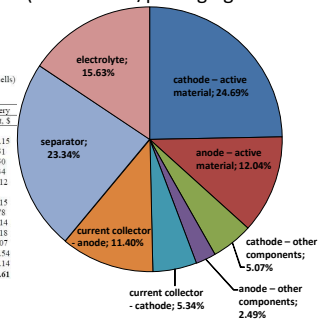
Non-active cell components

Non-active cell components comprise ca. 50% of cost and 33% of cell's mass (without can/packaging which in case of a steel can is another 33% of the cell's inner mass)

Table A-1. Cost of Materials in Cell Windings of a 40kW 4S-Cell Battery (24.7-Ah cells) That Employs the Gen 2 Cell Materials

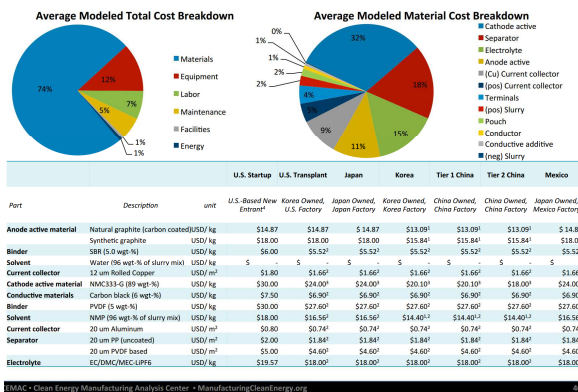
Type of Material	Quantity	Unit Cost	Cost
Cathode			
Active material ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$)	7,707 kg	20.52/kg	158.15
SEI-Co	0.367 kg	15.00/kg	5.51
Carbon black	0.367 kg	6.82/kg	2.50
PVDF binder	0.754 kg	10.00/kg	7.54
NMP binder solvent	5.383 kg	3.18/kg	17.12
Anode			
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	36.51 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. Lu, P.A. Nelson, ANL/DS



8

Non-active cell components



INMTC Clean Energy Manufacturing Analysis Center • ManufacturingCleanEnergy.org

9

Separators

Main purposes of the separator is:

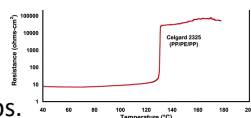
- Physical separation of electrodes (prevention against short circuit);
- Electric insulation (no electronic conductivity);
- Enabling electrolyte flow;
- Enhancing contact with electrode surfaces (wetting them with electrolyte) even at increased temperature or after the bending (rolling sheets to cylindrical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

10

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.



11

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.

12

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 15-30 μm range (depending on application). However, even very thin ones can decrease electrolyte conductivity few-fold (up to six-fold).

13

Separators

- Basic method of separator industrial manufacturing (80% of world production is made with that method) is so-called wet method. It consists in dissolving polymer in oil (solvent), extrude the foil with oil, stretch the foil and extract the oil. Extraction results in formation of porous structure (stretching can be performed after the extraction to obtain larger pores, if needed).
- Dry method consists in manufacturing of extruded foil, then laminating few layers (if separator is to be multilayer) maintaining temperature below melting point of all components. As a final step, material is stretched in order to obtain pores in it.

14

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.

15

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 10-30 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.

16

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.

17

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 its share, as well as PVP (poly(vinylpyrrolidone)) and nonfluorinated rubbers. Binder content can be in the 2-20% range, but usually do not exceed 10%.

18

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.

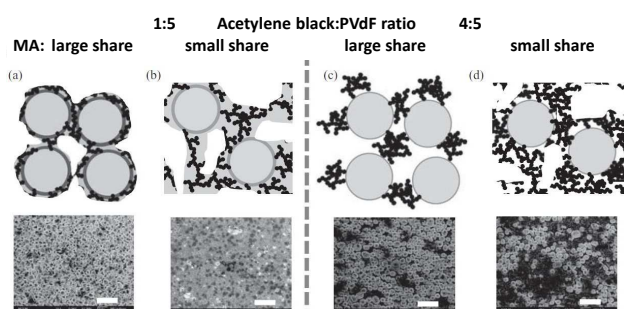
19

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.

20

Electrode mass



G. Liu, H. Zheng, X. Song, V.S. Battaglia, J. Electrochem. Soc. 159 (2012) A214.

21

Electrode binder solvent

Solvent for electrode binder is most commonly NMP (N-methylpyrrolidone), however in the past acetonitrile was used as well. Nowadays water is used more and more often (where it is possible). Solvent is needed to form a liquid electrode mass, in which all components (AM, additives, binders) will be mixed and uniformly distributed. It should allow for degassing (usually performed by ultrasounds), which means that it should allow for gas bubbles to form and escape easily. Solvent also should be cheap and easy to purify from dust and soluble impurities (so after evaporation its impurities would not be left in electrode mass).

22

Electrode binder solvent

Solvent should enable easy and free mixing of components and gas bubbles escape (low viscosity and Surface tension), but it should also be easy to evaporate after mass is applied to current collector foil.

It should not easily penetrate pores of electrode components (or it should be easy to remove from them). Solvent should be used in low amounts, so it would be easy to evaporate, but enough of it should be used in order to easily mix and properly disperse all components. Usually binder solvent is used in 75-125% range of final electrode mass (per dry mass).

23

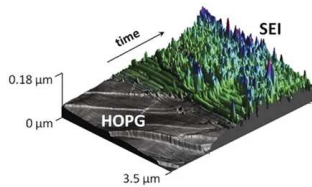
Casings

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.

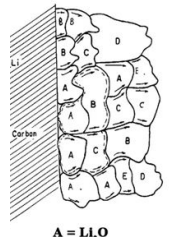
24

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.



A. Cresce, S.M. Russell, D.R. Baker, K.J. Gaskell, K. Xu, Nano. Lett. 14 (2014) 1405.



A = Li_2O
B = LiF
C = Li_2CO_3
D = Polyolefins
E = Semicarbonates

E. Peled, D. Golodnitsky, G. Ardel, J. Electrochem. Soc. 144 (1997) 1208.

25

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.

26

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.

27

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.

28

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.

29

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.

30