

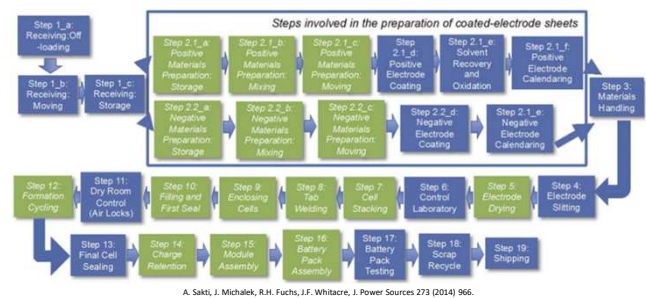
Batteries

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

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Li-ion cells manufacturing and operation

Manufacturing scheme



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 than 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).

7

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.

8

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).

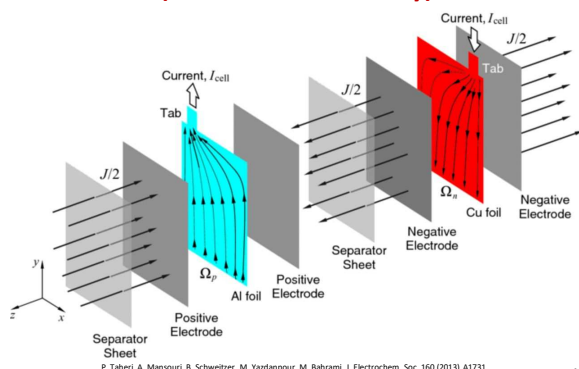
9

Dangers and cells safety testing

	UL																IEC		NEMA		SAE		UN		IEEE		JIS		BATSO	
Test Criteria/Standard	UL 1642	UL 2054	UL Subject 2271	UL Subject 2580	UL 2575	IEC 62133	IEC 62281	C18.2M, Pt2	J2484	PLIJS 38.3	IEEE 1625	IEEE 1725	JIS C8714	BATSO #1																
External short circuit	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Abnormal charge	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Forced discharge	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Crush	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Impact	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Shock	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Vibration	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Heating	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Temperature cycling	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Low pressure (altitude)	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Projectile	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Drop	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Continuous low rate charging						*	*	*	*	*	*	*	*	*	*															
Molded casing heating test								*	*	*	*	*	*	*	*															
Open circuit voltage								*	*	*	*	*	*	*	*															
Insulation resistance				*	*			*	*	*	*	*	*	*	*															
Reverse charge			*	*	*			*	*	*	*	*	*	*	*															
Penetration	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															
Internal short circuit test	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*															

10

Protection against overheating (and thermal runaway)



11

Protection against overheating

High temperature of the cell are the effect of high currents flowing through the cell. But the real danger is the local overheating (e.g. whole cell has 40°C on average, but at one point it is suddenly 90°C). It is enough for the overheating to last one second or so (until heat is dissipated), and electrolyte or electrode decomposition starts. LiPF₆ salt decomposes starting from 70°C, solvents are increasing their vapor pressure (potentially dangerous to the cell) ca. 100°C. All metal oxide cathodes have decomposition onset at 130-140°C. Cathode decomposition (called thermal runaway) is particularly dangerous – it produces a lot of heat (heating up and accelerating further decomposition of cathode) and oxygen (making ignition easier). That is why extinguishing methods based on cutting off the oxygen are so ineffective.

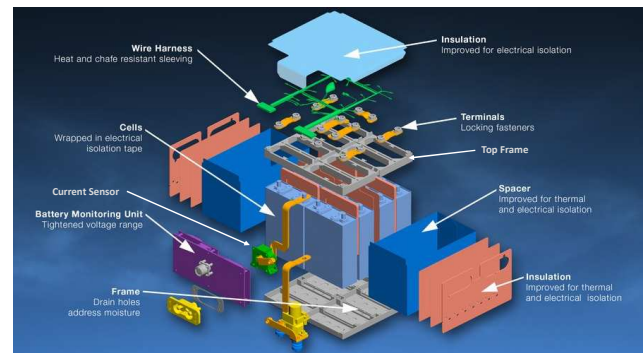
12

Protection against overheating

The risk of the local overheating has its roots in the cell design (no matter if it is cylindrical or prismatic one). All cells have their electrode tabs made of the extension of the current collector – and thus having its thickness. Even if the tab itself is thickened, then still close to the tab there is already higher current flow (electrons from the whole electrode sheet are going through the very narrow area, e.g. from the 20x20 cm electrode there is a tab of 1 cm width). Current is cumulated in a very narrow area and very thin one – collector have 8-16 μm . Thus, the neighborhood of the tab is the area with the highest risk of overheating and the potential ignition (initiation of the thermal runaway mechanism).

13

Protection against overheating



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14

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).

15

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.

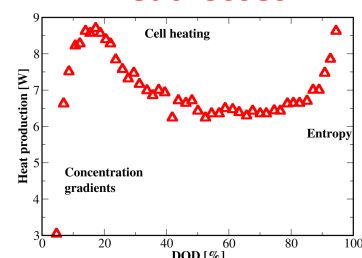
16

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.

17

Heat losses



L.O. Valéen, M.L. Shoemith, 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).

18

Cell operation and exploitation

In real life, in electric vehicles and hybrid electric vehicles (cars, trucks) and particularly in microhybrids, charging and discharging is carried out in a very chaotic way. Energy recuperation from braking occurs only while car breaks and it has to be engine braking. Discharge happens only when car accelerates and/or when car starts (with impulse). Charge and discharge current depends on various factors with various weights, including driving style of the individual driver, recuperation system efficiency, etc.

19

Cell operation and exploitation

One of the method for unification of measurements of duty cycles (uneven charge and discharge – for real conditions, not controlled or laboratory conditions) is use of the mean current of such cycle. Unfortunately such method does not account for differences between intense and mild cycles.

Method that takes that difference into account is a duty cycle eccentricity method (DCE). It calculates ratio between standard deviation of current from the mean current:

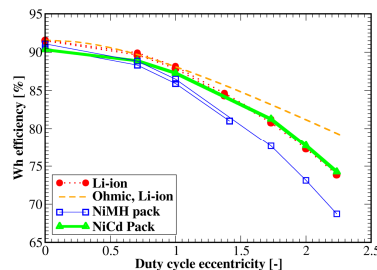
$$DCE = \frac{\sqrt{I^2 - \bar{I}^2}}{\bar{I}}.$$

20

Cell operation and exploitation

3 Ah cell discharge with 3.3C (10 A) mean current (variable), with a steady charge with 1C (3 A) current. Efficiency dependence of discharge conditions changes rapidly.

„Ohmic” is a data set for ideal system (efficiency depends exclusively on Coulombic efficiency, so it omits diffusion effects and electrode reactions).

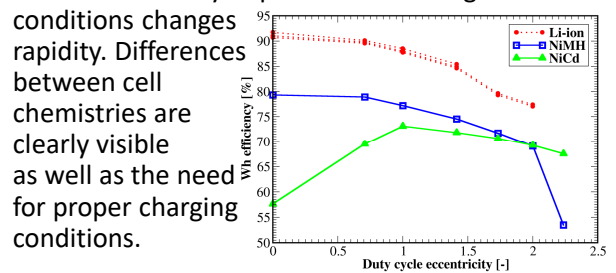


L.O. Valdeen, M.I. Shoosmith, The effect of PHEV and HEV duty cycles on battery and battery pack performance, PHEV 2007.

21

Cell operation and exploitation

3 Ah charge with 3.3C (10 A) mean current (variable), with a steady discharge with 1C (3 A) current. Efficiency dependence of charge conditions changes rapidly. Differences between cell chemistries are clearly visible as well as the need for proper charging conditions.



L.O. Valdeen, M.I. Shoosmith, The effect of PHEV and HEV duty cycles on battery and battery pack performance, PHEV 2007.

22

Cell operation and exploitation

On both figures (on two previous slides) one can see advantage of Li-ion cells over previous generations of batteries. Insufficiency of nickel-based cells at higher eccentricities in high rate charging is also visible. Nickel-based cells operation quality strong dependence of favorable charging (mostly) conditions can be also observed.

All this results in usefulness of new cell chemistries to EV and HEV applications (where there is high eccentricity of duty cycles).

23