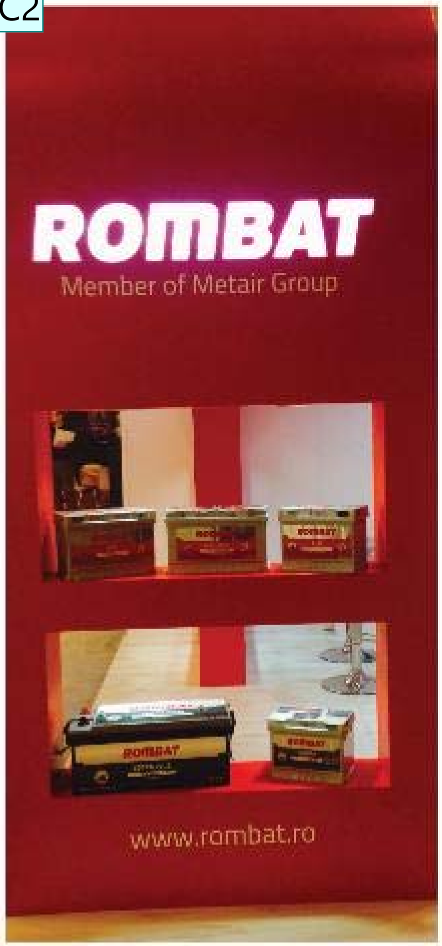
EC2



SuperEndurance Technology

ROMBAT

EuroNanoForum 2019

New challenges for the lead acid storage and automotive starter batteries industry: high efficiency energy conversion and reduced environmental impact

ROMBAT
Member of Metair Group

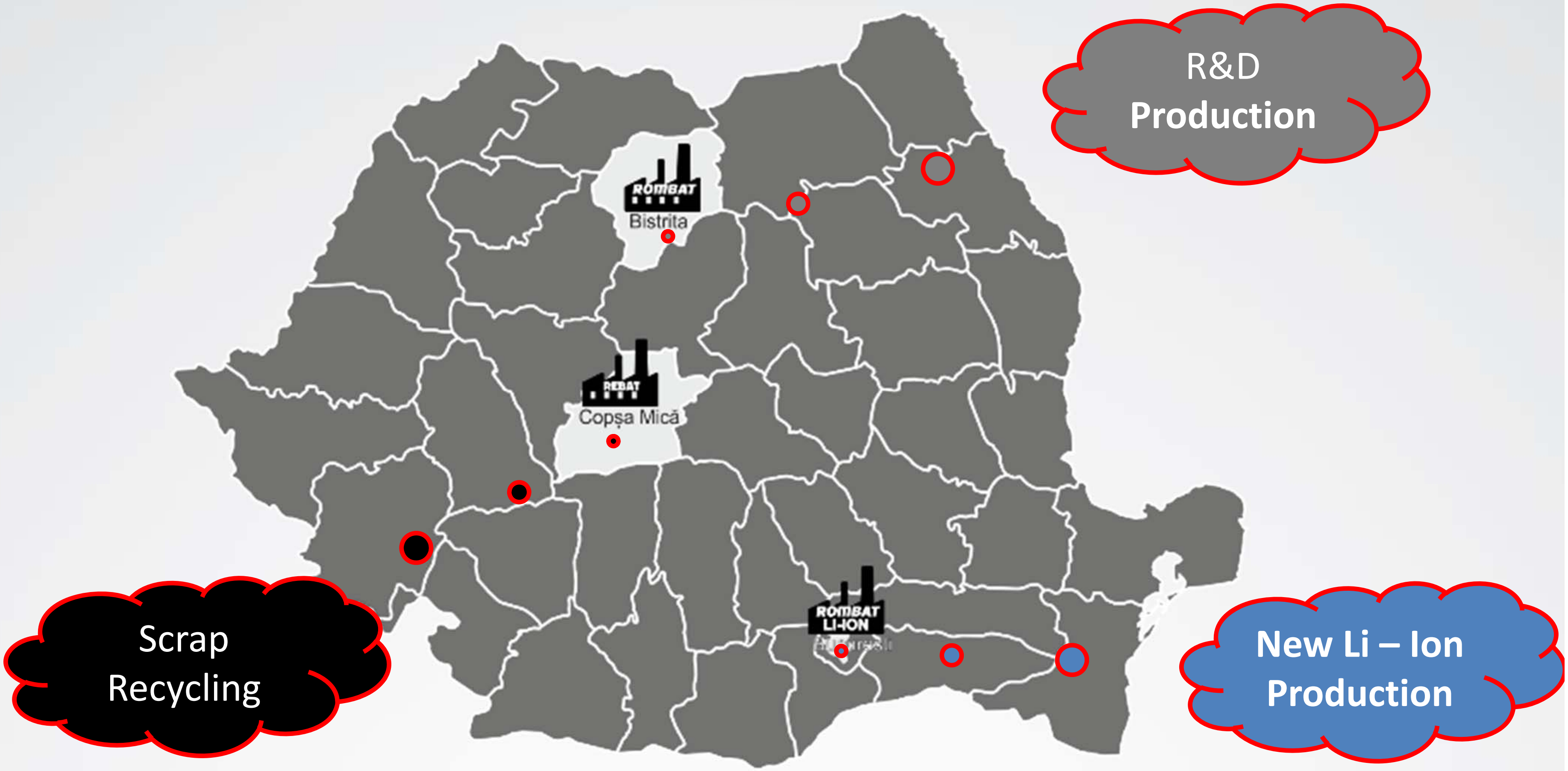
Slide 1

EC2 Please, let me introduce my company is ROMBAT S.A. in Bistrita, at first:
Was founded in 1980, as „ACUMULATORUL” Bistrita, as part of a state owned industrial platform CICM in Bistrita.
Today is the sole Lead Acid Starter Battery Manufacturer in Romania.
With more de 2.3 million batteries production sold in 2018
Member of South African MIB Group – owned by METAIR Investment Ltd., since 2012

My name is, Ernest Csapo – Martinescu and am currently Senior Technical Advisor at ROMBAT Technical Department.
My professional background is Electrical Engineering, and I am Ph.D in Electrical Machines, Drives and Apparatus, with more than 25 years experience in Lead Acid Batteries Design and Development.
Ernest Csapo; 24.06.2019

EC3

Location



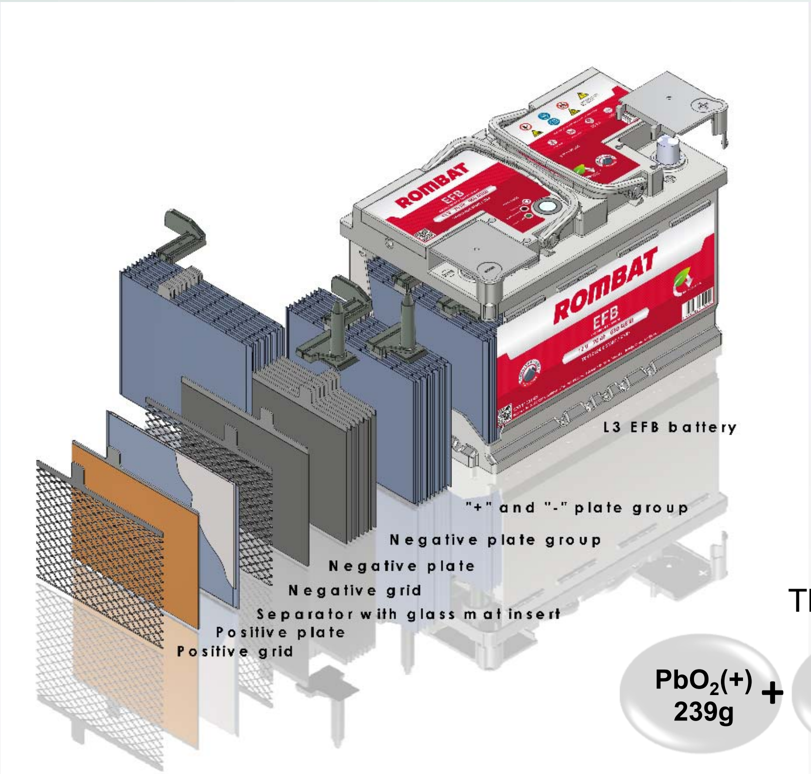
Slide 2

EC3 ROMBAT in Bistrita is located on Northen part of Romania, at the foot of the East Carpathian Mountains.
There are 3 batteries production plants, one plastic injection plant, laboratories and R&D department.
In the center of the country, at less than 200 km distance, is situated REBAT Copsa Mica, ROMBAT's scrap batteries recycling plant, delivering reused refined lead (Pb) and lead alloys for the new batteries production.
A new Li – Ion prototype batteries assembling factory was founded at Bucharest, as a new start in developing motive power Li – Ion Batteries for EV and other uses.

ROMBAT is manufacturing a large range of Lead Acid automotive starter batteries:
Standard Flooded Batteries technology – vented types for
Cars
Heavy Duty (Trucks, Buses)
EFB Enhanced Flooded Batteries – vented types for S&S microhybrid cars
AGM Absoptive Glass Matt, Valve Regulated Lead Acid batteries – sealed types for S&S premium cars
A 12 million EURO investment launched for a new Li – Ion Batteries and Cells manufacturing factory was founded last year at ROMBAT Bucharest site. Based on 2 chemistries:
NMC – Lithium Nichel Cadmium Oxyde type cells - 30 Ah/ 3.65 V
LFP – Lithium Iron Phosphate (Ferrophosphate) type cells - 20 Ah/ 3.2 V
Ernest Csapo; 24.06.2019

EC4

12 V Lead Acid Battery Design



Lead Dioxyde PbO_2 (+)

Spongious Lead Pb (-)

Electrolyte

The electrochemical reaction (molar based):

PbO_2(+)	+	Pb(-)	+	$2H_2SO_4$(elyt)	⟷	$2PbSO_4$	+	$2H_20$(+)	+	$2e^-$
239g		207g		2X98g		2x303g		2x18g		2x26,77Ah

Electrochemical equivalents (netto):

- PbO_2-> 4.464 g/Ah
- Pb-> 3.866 g/Ah
- H_2SO_4 -> 3.66 g/Ah

$PbSO_4$ -> 11.318 g/Ah

H_2O -> 0.672 g/Ah

EC4 An example of a ROMBAT EFB battery for modern Micro Hybrid Start & Stop cars is presented.
There are quantitive relations between active mass amount – lead dioxyde (positive plate) and spongios lead (negative plate).
The active mass is partially used as „energetic" layer – the rechargable part of active mass is around 50 % only.
The other 50 % of active mass part is used as „conductive scheletton" for the „energetic layer" connecting the active mass to the lead grids.
Ernest Csapo; 24.06.2019

EC5

New challanges – Lead Acid Starter Batteries

Requirements for Flooded Batteries – EN50342-1: 2015

- ❑ Effective 20 h Capacity at 25 °C – Statistical Approuch (Mean & Standard Deviation)
- ❑ Cranking Performance at -18 °C – requirement $t_{6V} \geq 90$ s
- ❑ High Current Discharge at Low Temperature at -18 °C – requirement $U_{30s} \geq 7.2$ V
- ❑ **Water consumption H_2O at +60 °C – requirements W3 ≤ 8 g H_2O / Ah for 42 days**

Requirements for Micro Hybrid Batteries – EN50342-6: 2015

- ❑ **2 % DoD – Microcycling PSoC (85 %SoC) at 25 °C / 8000 cycles**
- ❑ Dynamic Charge Acceptance – requirement ≥ 0.1 A / Ah
- ❑ 17 %DoD – Endurance Cycling PSoC (85 %DoD) – requirements 9/15 /18 weeks
- ❑ 50 %DoD – Endurance Cycling after Deep Discharge – requirements ≥150/240/360 cycle

New Requirements for S & S (Start & Stop) – EN50342-6: 2019 (draft)

- ❑ **2 % DoD – Microcycling PSoC at +40 °C / 16000 cycles & 32000 cycles**
- ❑ **New KLT at +75 °C – requirement Water Consumption Wx ≤ T.B.D.**

Slide 4

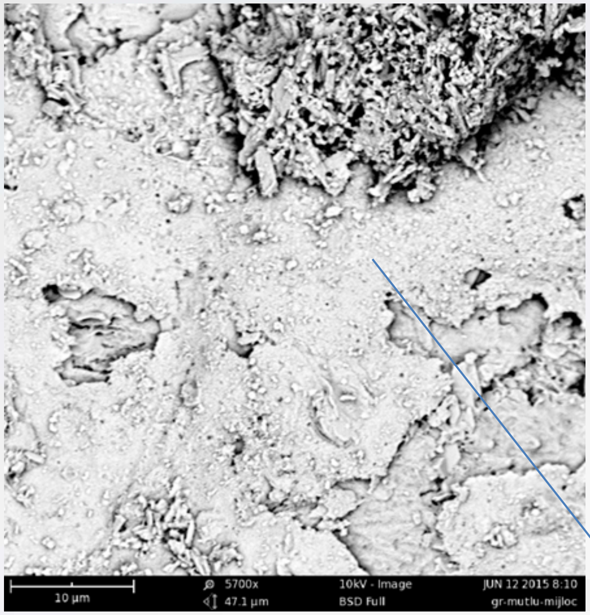
EC5

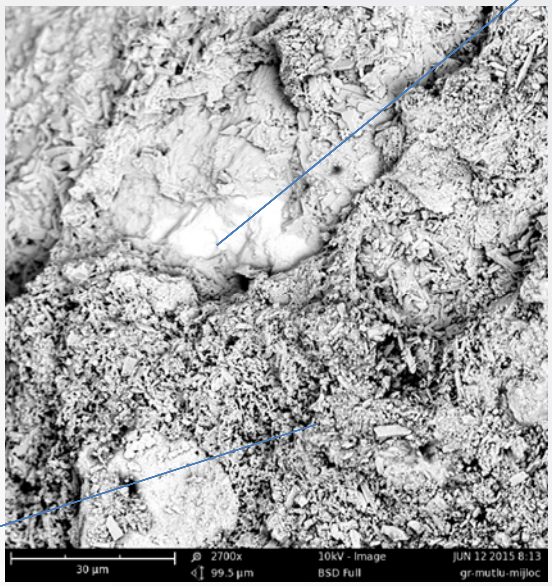
Only two examples of strong challanges:
The water consumptions H2O –
test temperature was increased from 60 oC to 75 oC (battery immersed in waterbath)
2) Very high microcycling endurance requirements –
test temperature increased from 25 oC to 40 oC, and
number of 2 % DoD microcycling endurance resistance increased from 8,000 cycles to double (mandatory) 16,000 cycles or more.
Ernest Csapo; 24.06.2019

EC6

Corrosion layer curred plate

Bad contact





Good contact

Slide 5

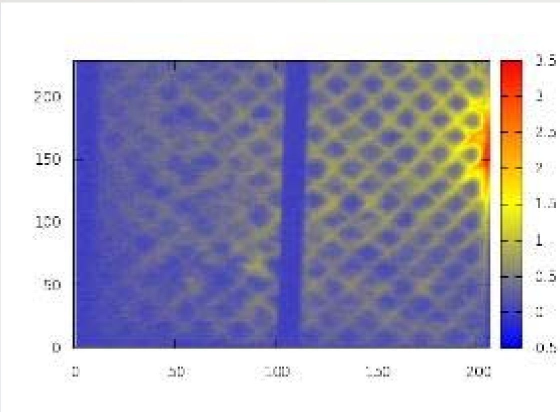
EC6

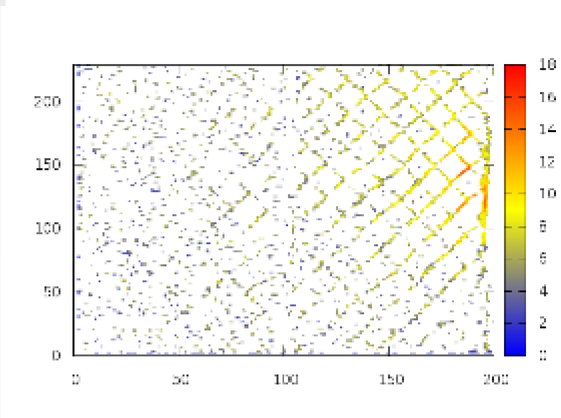
A critical item in the Lead Acid Batteries manufacturing is the corrosion layer between lead alloy grid surface and the curred / formed active mass.
Good corrosion layer, covering complete the grid surface by Lead Oxyde / Sulphate interface, conduct to
Reduced electrical internal resistance of plate
High starting performance – Could Crank Current (A)
In case of the grid surface is not completly covered (glossy zones) the active mass is not optimally used,
risc for early grid growth (potential shortcircuit inside cells) and
corrosion (ribs crossection reduced or interrupted)

This phenomennon starts from the pasting process, as shown in the figure.
Good contact – the grid is completely covered by Lead oxyde crystals
Bad contact – glossy zones means lack of corrosion layer on curred plates
Ernest Csapo; 24.06.2019

EC7

Current Distribution in Commercial plates





j (A/mm²) – current density distribution

Mathematical model

Propagation of the thermal wave in a homogenous environment, in the presence of a heat per volume and unit time q is:

$$\frac{\partial T}{\partial t} = \propto \Delta T + \frac{1}{c_p \rho} q \qquad (1)$$

$T = T(x, y, z, t)$ is the temperature

q - heat per volume and unit time

$\propto$ - thermal diffusivity: $\propto = \frac{K}{c_p \rho}$

K - thermal conductivity

c_p - specific heat capacity

ρ - density of the material

Δ - Laplace operator: $\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

The Laplacian of temperature distribution is

$$\Delta T = \frac{1}{\propto} \frac{\partial T}{\partial t} - \frac{1}{K} q \qquad (2)$$

The power dissipated by current per volume unit, $p = P / V$ is $p = j^2 / \sigma$

The relation between current density and conductivity is $j = -\sigma \varepsilon$

The Laplacian of the temperature distribution is

$$\Delta T = \frac{1}{\propto} \frac{\partial T}{\partial t} - \frac{j^2}{\sigma K} \qquad (3)$$

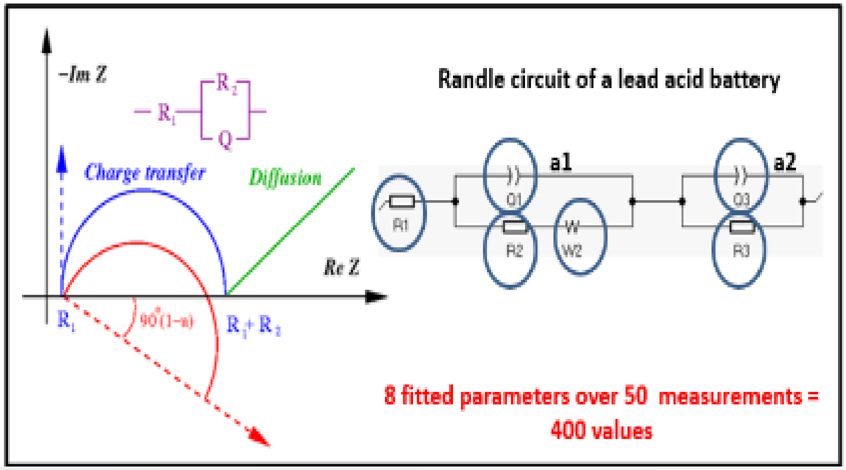
The current density can be computed as

$$j^2 = \sigma K \left(\frac{1}{\propto} \frac{\partial T}{\partial t} - \Delta T \right) \qquad (4)$$

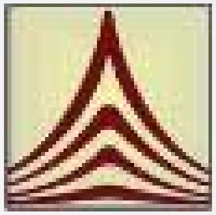
Slide 6

EC7 In cooperation with INCDTIM Cluj – Napoca, the current density distribution inside of plates is identified by using Thermographical analysis method.
Based on this data, a new grid design was ellaborated, and implemented in a new battery application.
The succesive Thermal Images stored in the computer, based on mathematical model issued by the researchers, allows the calculation of the local current density in the plate.
Very different current densities in the grid are noticed.
High current densities figures in the top area near the flag.
Low densities on the base of the plate.
This is the reason why the active material of plates are analysed on tree zones:
On the top
In the middle
On the bottom
The aim is to uniform the current density and active mass efficiency on the whole plate surface and Optimise the grid design according to the current density measured.
Ernest Csapo; 24.06.2019

Electrochemical Impedance Analysis



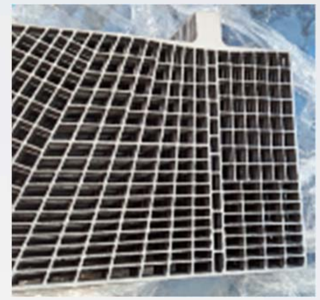
- Battery = electric circuit
- Frequency-dependent impedance = fit to circuit elements
- The value of each circuit element depends on the SOH of the battery

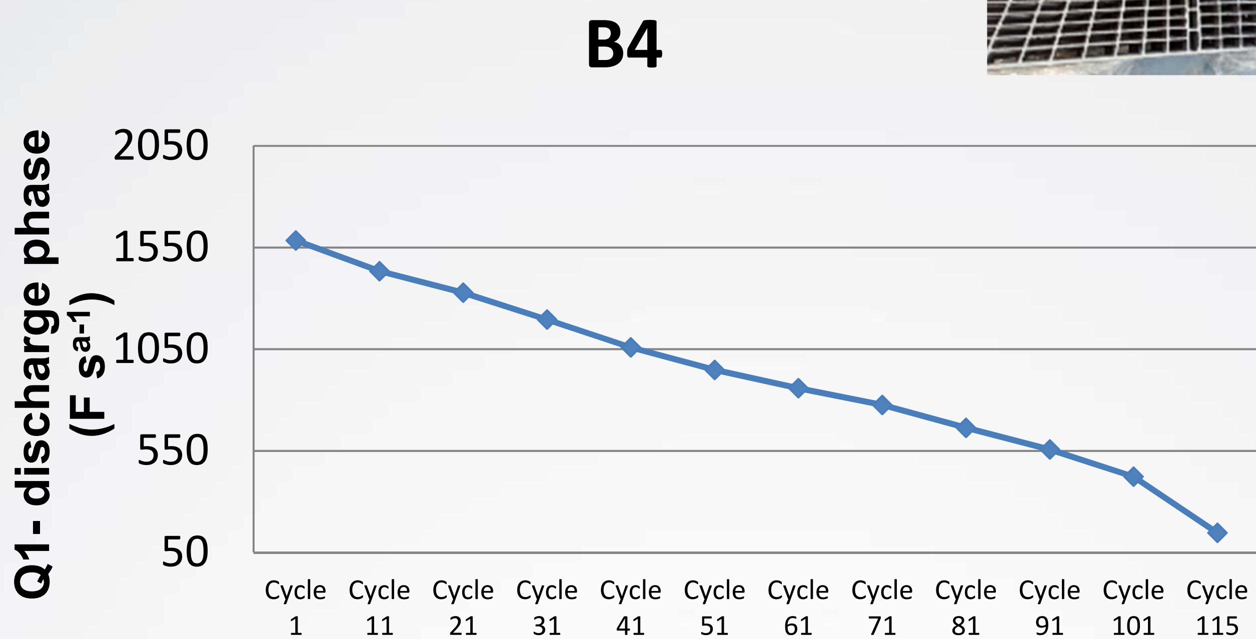


- T. Murariu, C.Morari "Time-dependent analysis of the state-of-health for lead-acid batteries: An EIS study" J ENERGY STORAGE, 21, 87 (2019) – INCDTIM Cluj-Napoca, RO

EIS data on newly designed grids

Example: dependence of the CPE element at 75% SOC as a function of aging cycles for a newly designed battery plate





EC8

Another Research and Product Development, supported by INCDTIM Cluj – Napoca, is based on the individual cells and batteries EIS (Electrical Impendance Spectroscopy) characterization.
The most relevant parameter of the EIS electrical equivalent circuit is the CPE (constant phase element) Q1.
A direct quasi linear dependance between battery aging and Q1 was identified.

The evolution of Q1 (F sa-1) is the most relevant parameter for the battery aging.
The new design can be assesed and development duration and costs dramatically redused.
Ernest Csapo; 24.06.2019

EC9

Conclusions

- With a 160 years of history behind, the Lead Acid Batteries are used actually for starting the Internal Combustion Engines of Automotive Vehicles
  - For medium term – in the next 15 – 20 years – they are still necessary
  - Based on market figures, in 2018, the new Start and Stop technology is used for more than 85 % of the new cars – in 2030 will be estimated around 50 % EV
- New European Norms enforce new quality requirements and major restrictions on environmental impact
  - The Research trend is headed to Active Mass Improvements by using Ingredients (crystallisation centers, conductive carbon additives)
  - The Grid Design has a relevant role in Electrical Current Collection from the Active Mass and leads to increase of Cycling Endurance Lifetime
- New Investigation Methods are applied for quick parameters analysis and product characterization – for early design quality asessments

EC9 In conclusion:

the lead Acid Battery chemistry, known for 160 years, are facing today the hardest challenges on survival.

Lead ban on European market – heavy metall, exemption based automotive batteries manufacturing only allowed, and subjected to periodically review by the EC.

New customer performance required – increased operational temperature (60 oC -> 75 oC), reduced water consumption, double number of endurance cycles (microcycling)

Lead Acid Batteries are the optimal solution for ICE startup

High startup performance at low temperature

No explosion risk – liquid aquaeous electrolyte

Very good cooling in case of high current cycling – high specific heat of the electrolyte

100 % reclycling – lead, plastic material – circular economy, reused prime materials for new batteries production

Today market figures 85 % of OEM (new cars) are microhybrid S&S type.

The OEM represents 18 % - 20 % of the total lead acid batteries market in Europe.

The trend is to

Hybrid cars,

Plug in Hybrid and

EV, forcasted figure in 2030 of EV-s in the OEM volume (new cars) is around 50 %

Mid term perspective: in the next 15 -20 years the Lead Acid Batteries will be used, so any improvement of lead use effciency (only 50 % of active mass is forming the energetic layer) and CO2 greenhouse gas makes sens.

Very high improving potential for the negativ plate technology (carbon black, acetylene black, nanotubes)

Ernest Csapo; 24.06.2019

Contact details

Ernest-Elöd Csapó-Martinescu

Ph.D. in Electrical Engineering
Senior Technical Adviser
Product Design & Development

ROMBAT

			Drumul Cetăţii, nr. 4, 420129 Bistriţa, România	
Certified according			Tel:	+40 374 170364
ISO 9001:15			Fax:	+40 263 234010
IATF 16949:16			ernest.csapo@rombat.ro	
ISO 14001:15			www.rombat.ro	
OHSAS 18001:07			www.facebook.com/baterii.rombat	

https://www.euronanoforum2019.eu/speaker/e-csapo-martinescu/

THANK YOU!

MULTUMIRI