MAT4BAT

Advanced materials for batteries

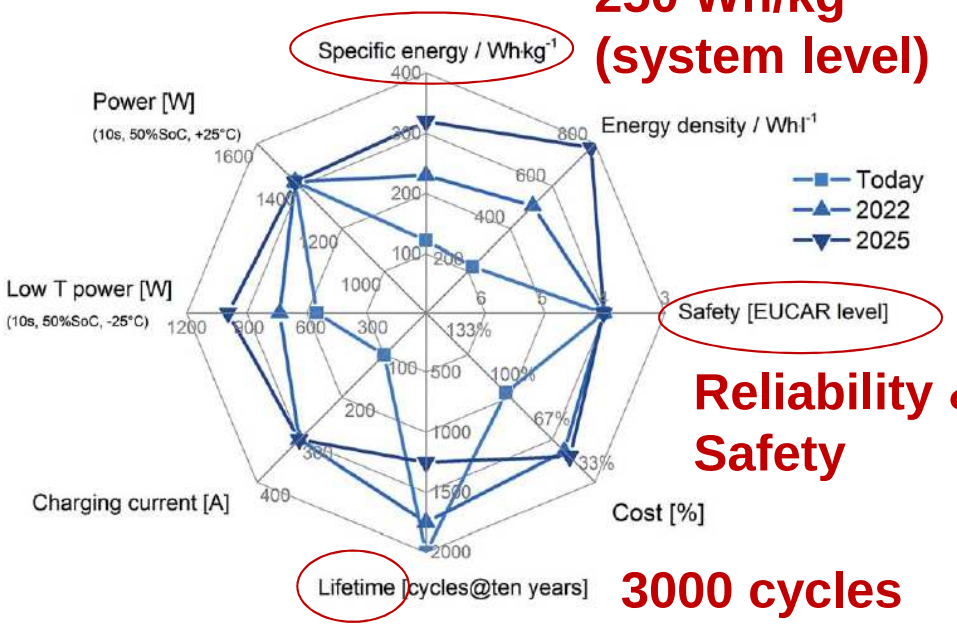
European workshop on nanotechnologies & advanced materials for batteries

Context: Energy storage for xEV

- **Battery storage** for electrified vehicles
  - Boost with Li-ion batteries introduction
  - Still limiting parameters for large scale commercialization
    - Lifetime
    - Driving range
    - Quality & safety
    - Cost
  - Affordable economical business plan for OEMs strongly depending on storage

- **Understanding and control of battery ageing mechanisms is the key**
  - Extending battery lifetime
  - "Smart" BMS and charging modalities implementation

- **Li-ion cell is the core component**
  - Design and process including materials & electrodes
  - Highlighting of ageing mechanisms
  - Advanced materials integration could help increase energy density and lifetime



D. Andre et al., Future generations of cathode materials: an automotive industry perspective, *J. Mater. Chem. A.* 3 (2015) 6709–6732

Objectives

16 Ah Commercial C/NMC cell

1. *Assessing performance, lifetime and safety of batteries*
   - Adress **all critical ageing mechanisms** associated to **NMC/G technology** (SoA commercial cells GEN#0)
   - Implement **advanced testing tools and procedures**
   - Define **critical charging modalities** for a battery system during practical use

2. *Development of advanced materials for safe and ageing resistant batteries*
   - Implement **3 new generations of Li-ion cells** from liquid, to gel and then to solid-state electrolyte
   - Manufacture and test **large cells (> 10 Ah)** in order to validate best technologies against quantified objectives

	GEN#1	GEN#2	GEN#3
ENERGY	150 Wh/kg	200 Wh/kg	250 Wh/kg
DOD	80 %	80 %	80 %
LIFETIME Standard charging	2000 cycles	3000 cycles	4000 cycles
LIFETIME Fast charging	1500 cycles	2250 cycles	3000 cycles
SAFETY	Qualitative information (ex. Nail test, crush test, overcharge according to standard protocols)		

(-) material	Synthetic graphite		
(-) formulation	Graphite-graphene-NTC blends		
(+) material	NMC	Li-rich	Li-rich
(+) formulation	Water-based formulation	Water-based formulation	Optimized formulation
Separator	Microporous separator	PVdF-HFP membrane	Solid polymer electrolyte
Electrolyte	Advanced liquid	Optimized gel	
Packaging	Standard soft	Soft composite	« Smart »

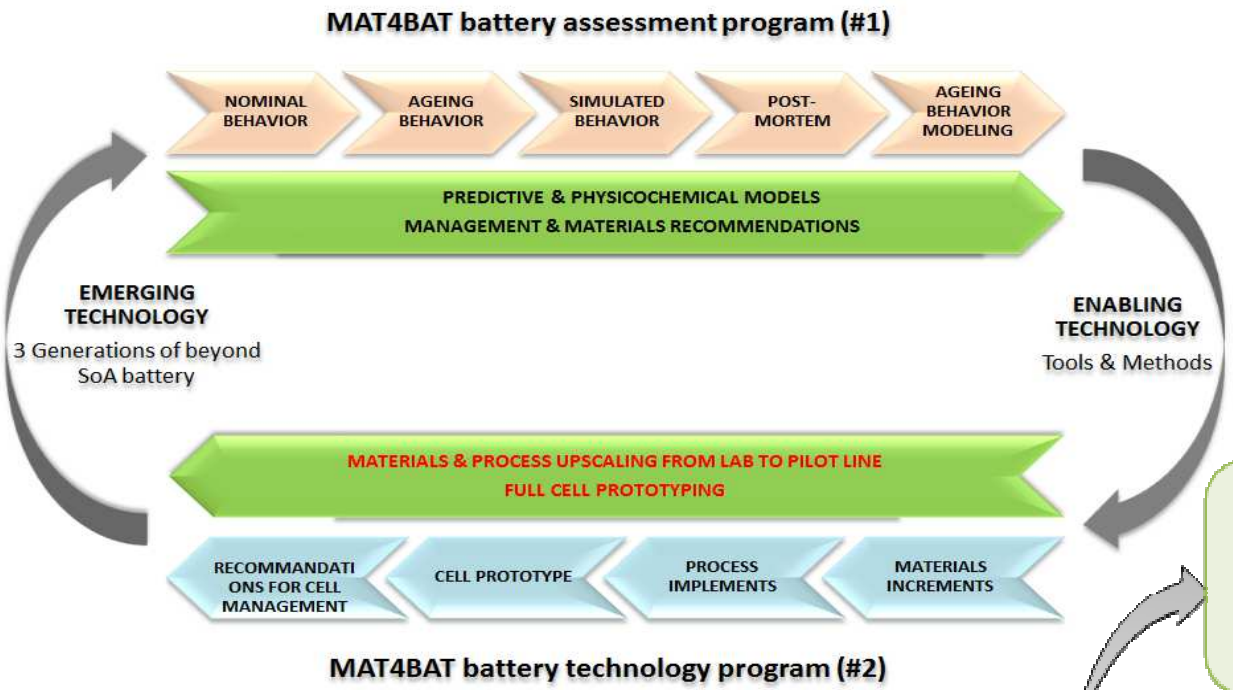
Mat4Bat consortium & information

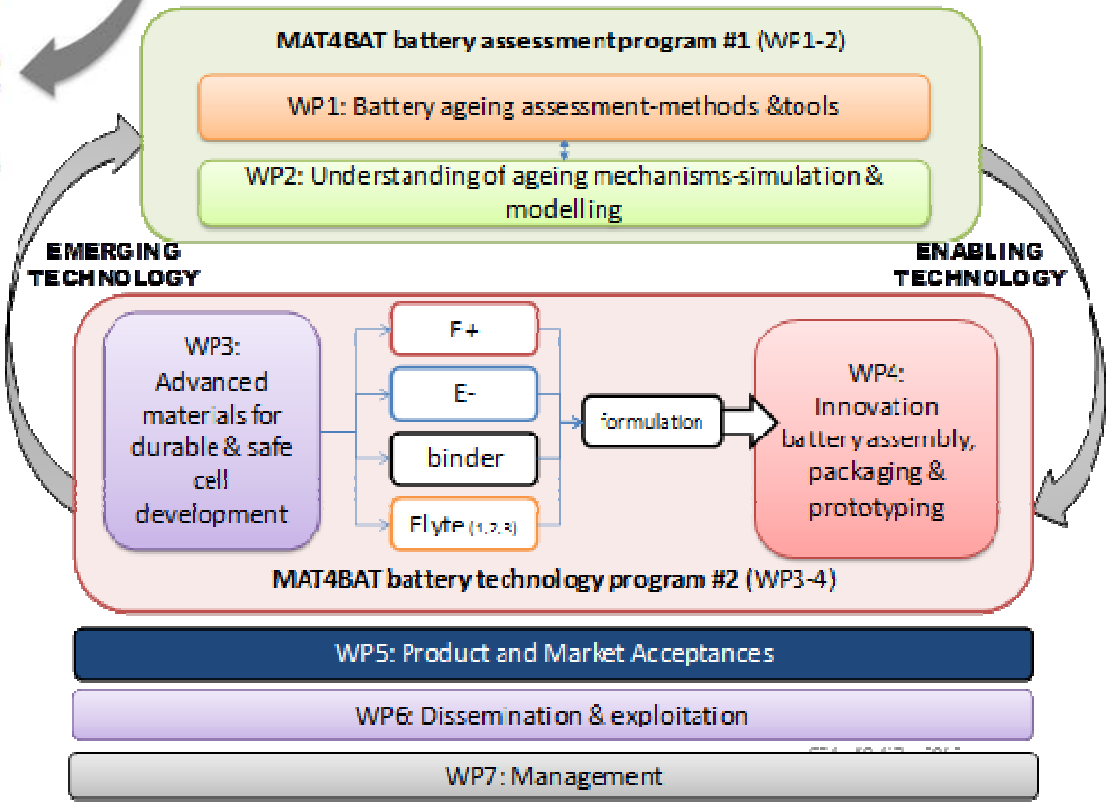
- 4 Large groups
  - Kurt Salmon
  - SOLVAY
  - IMERYS Graphite & Carbon
  - RENAULT
- 2 SMEs
  - Solvionic
  - DIRECTAPLUS
- 5 RTOs
  - ZSW
  - cea
  - CIC energiGUNE
  - vito
  - IK4 CIDETEC
- 5 Academics
  - macro PRAGUE
  - Newcastle University
  - EIGSI ÉCOLE D'INGÉNIEURS LA ROCHELLE
  - KIT Karlsruhe Institute of Technology
  - INSA LYON

Note: CEGASA participation to MAT4BAT project was ended in March, 31st 2015

- Grant agreement # 608931
- Time:
  - Duration: 42 months
  - Starting date: 01/09/2013
  - End date: 28/02/2017
- Budget:
  - Total cost: 11 443 522 €
  - EU contribution: 8 191 959 €
- Project website:
  - http://mat4bat.eu/

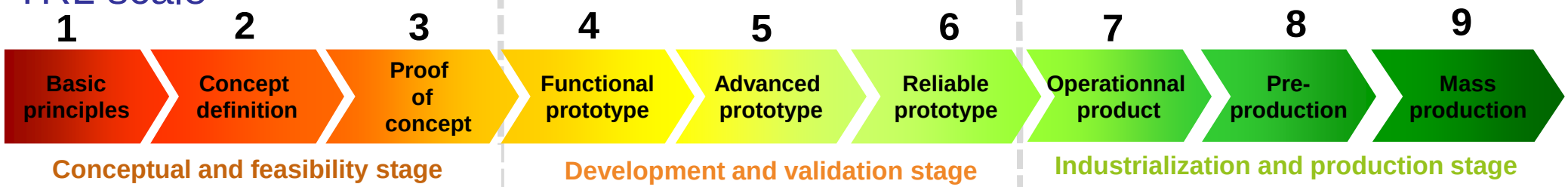
Implementation





Material & process innovation

- TRL scale



NMC cathode material

Liquid Electrolyte

Synthetic graphite anode

PVdF water-based binder → *GEN#1 cells*

Li-rich cathode material → *GEN#2A cells*

Gel polymer electrolyte → *GEN#2B cells*

Composite packaging

Solid-state polymer electrolyte → *GEN#3 cells*

- Risk management

Development delays + low maturity components for Gen#2 and #3

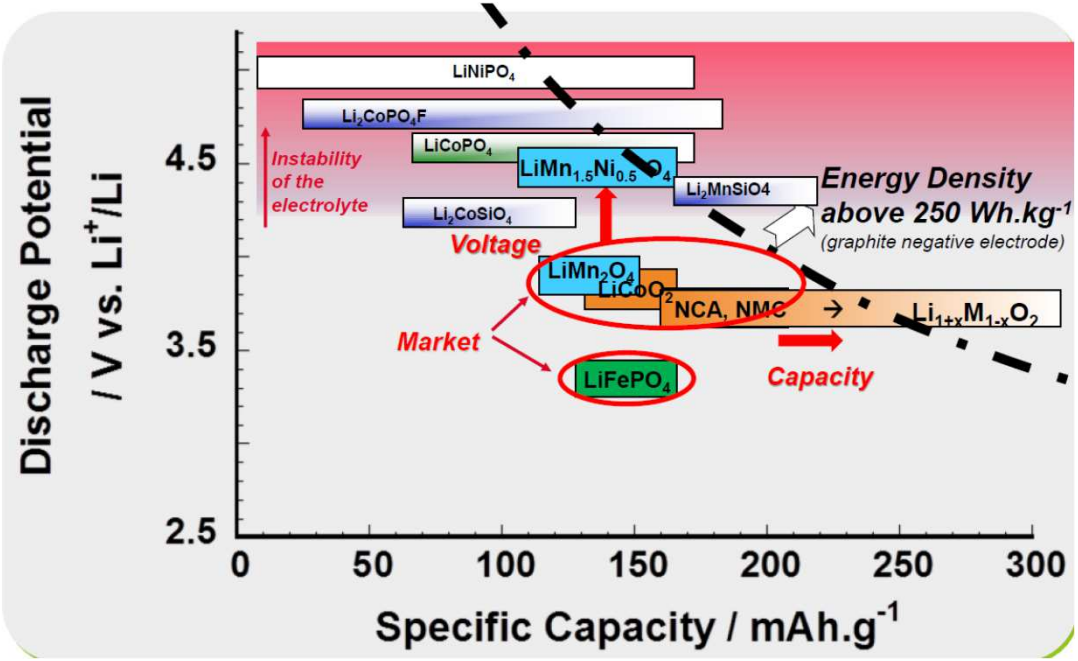
→ Smaller material increment & lower capacity cells

Advanced cathode materials

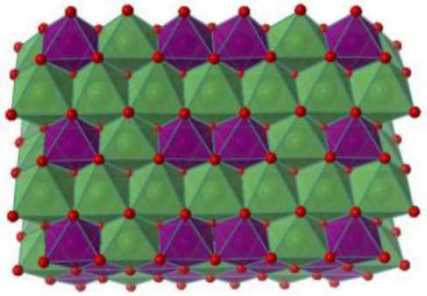
- Search for new cathode materials enabling **higher energy density**

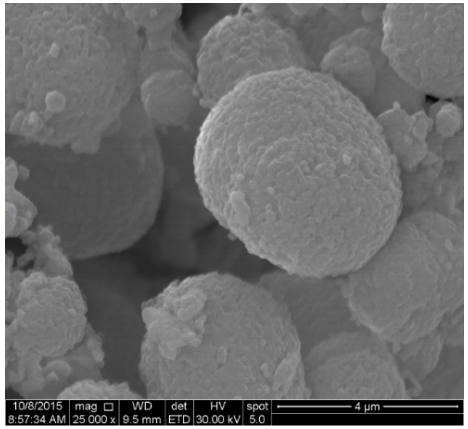
- **Interest for Li-rich materials $Li_{1+x}M_{1-x}O_2$** (0<x<1/3 ; M = Mn, Ni,…)
  - High specific capacity **> 250mAh/g**

  (vs. 180mAh/g for NMC)
  - High energy applications > 250-300Wh/kg
  - Low cost materials



- **Main issues to be solved**:
  - Structural mechanism understanding
  - First high irreversible specific capacity
  - Gas generation issue during 1st cycles
  - Voltage decay upon cycling
  - Thermal stability & power perfs improvement





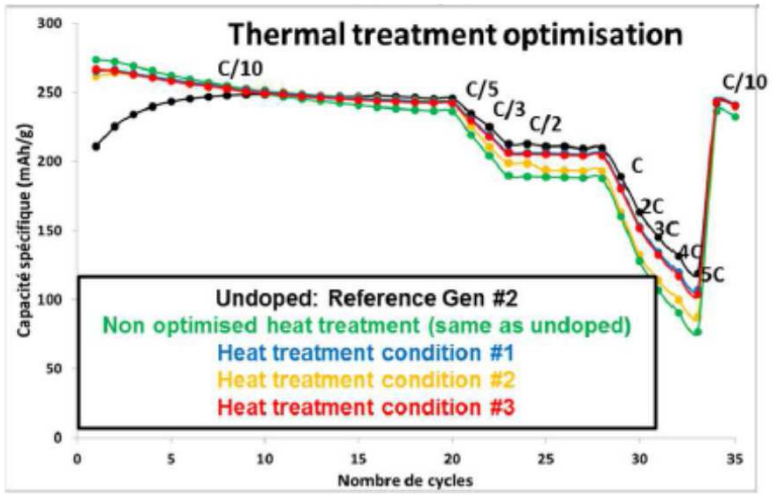
Advanced cathode materials

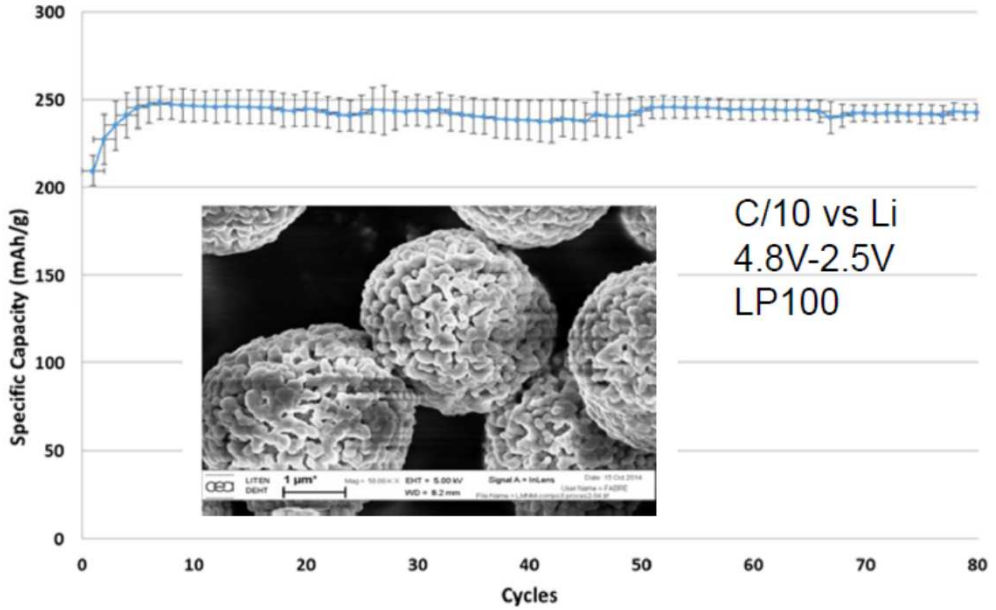
- First screening of **synthesis method and conditions**

- **Optimization of Li-rich material composition** (doping)
  - DOE for process optimisation (co-precipitation)
  - DOE composition optimization

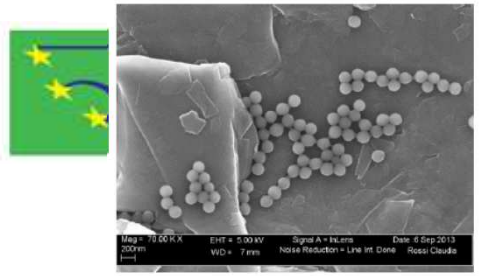
- Attempts to create **graphene coatings**

- Selected material was **upscaled to 10 kg** for prototypes manufacturing
  - Stable and reproducible performances compared to lab-scale batches

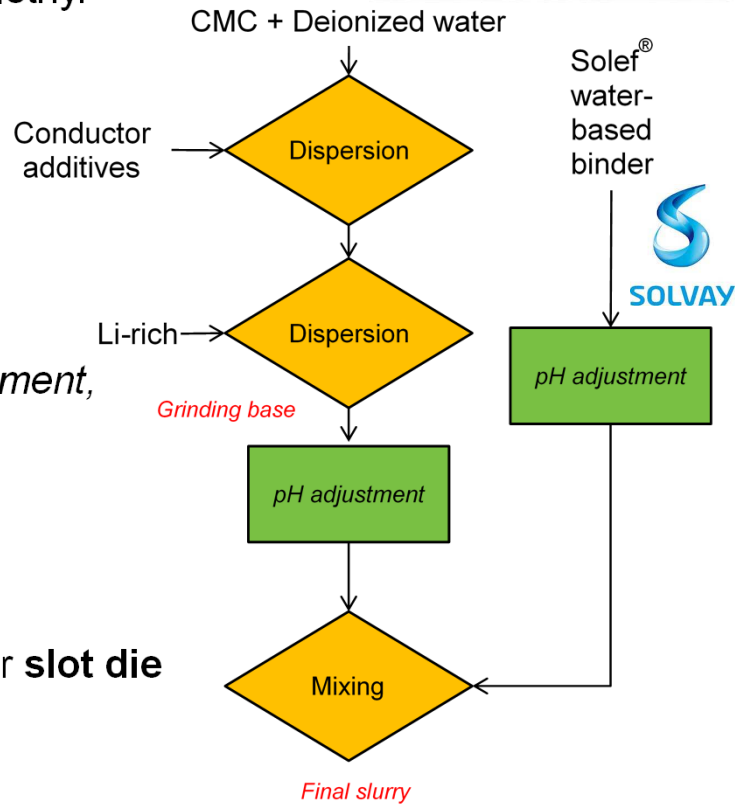




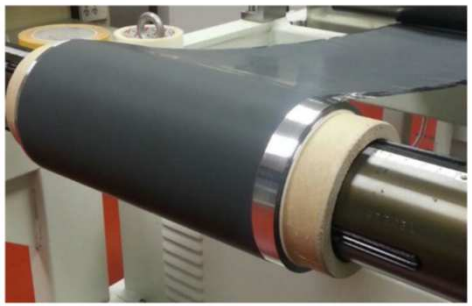
Electrode manufacturing



- **Technological issues** associated to electrodes
  - Environmental, health and costs concerns associated with the use of N-methyl pyrrolidone (NMP) → ***Water-based slurry manufacturing***
  - **High sensitivity of lithium metal oxides (NMC, Li-rich)** towards water
    → *pH control to avoid alkaline slurries / aluminium surface corrosion*
  - Binder optimization
    → *SOLVAY PVdF-based latex implementation*
  - Scale-up development
    → *Formulation development, stability control and coating ability assessment, mechanical properties*
- **Process development** in Mat4Bat
  - **~ 1kg slurry batches**
  - Slurry pH adjustment and monitoring
  - Electrodes successfully coated using **comma-bar reverse-roll coating** or **slot die coating** (several tens of meter-long electrodes)

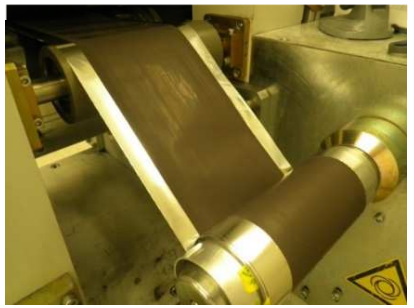


Gen#1 - NMC – slurry mixing



Gen#1 - NMC – final cathode roll

Gen#2 - Li-rich - wet coating



Gen#2 - Li-rich - calandering

Prototype manufacturing

- Beneficial use of **battery manufacturing platforms** (Cegasa, CEA, Cidetec, KIT) to assess material development at cell level

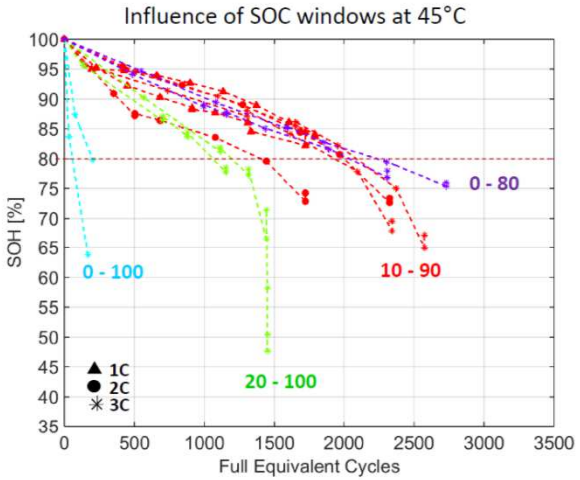
	Material development	Lab-scale cells	Component up-scaling	Large cells manufacturing	Ageing evaluation
GEN#1	☑	☑	☑	☑	☑

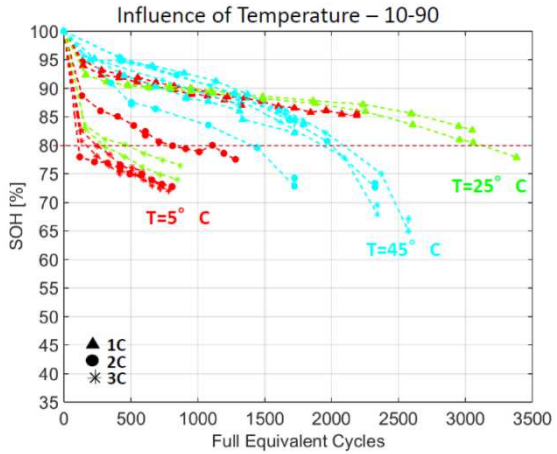
GEN#1: High capacity NMC / graphite cells, SoA technology, water-based electrode process

17 Ah nominal capacity
~150 Wh/kg

- Prismatic soft packaging, 140 mm x 230 mm
- Stack cell

Cell stacking-winding unit





	GEN#1	
ENERGY	150 Wh/kg	✔ 157Wh/kg @ 1C/1C, 25° C
DOD	80 %	
LIFETIME Standard charging	2000 cycles	✔ 2000 cycles @ **1C**/1C, 45° C, 10-90% **3000 cycles @ 1C/1C, 25° C, 10-90%**
LIFETIME Fast charging	1500 cycles	✔ 1500 cycles @ **2C**/1C, 45° C, 10-90% certainly > @ 25° C *but not tested* ✘ *@ 3C → < 500 cycles both @ 25° C and 45° C*

A. Kvasha, et al., Development of Large Format NMC-Graphite Lithium Ion Pouch Cell with Aqueous Processed Electrodes, *ECS Trans.* 73 (2016) 325–330

Prototype manufacturing

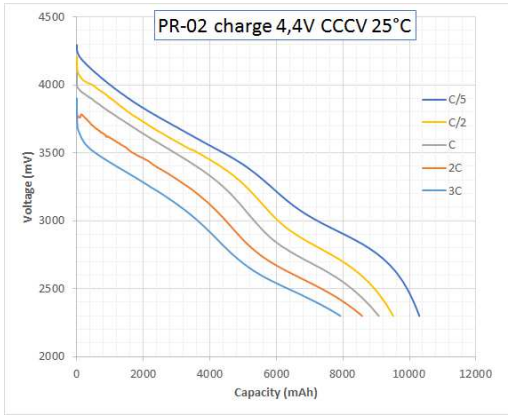
- Beneficial use of **battery manufacturing platforms** (Cegasa, CEA, Cidetec, KIT) to assess material development at cell level

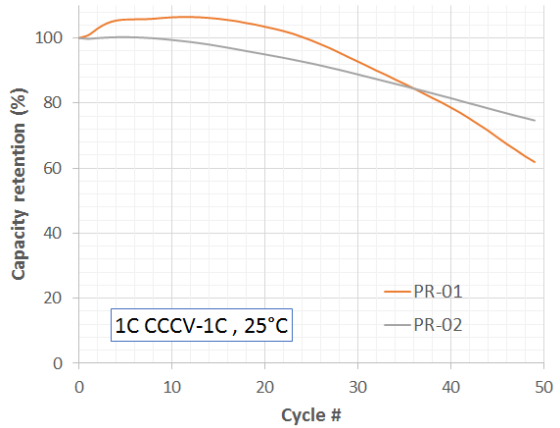
	Material development	Lab-scale cells	Component up-scaling	Large cells manufacturing	Ageing evaluation
GEN#1	☑	☑	☑	☑	☑
GEN#2A	☑	☑	☑	☑	*To be continued*
GEN#2B	☑	☑	*To be continued*		
GEN#3	☑	*To be continued*			

GEN#2A: High capacity Li-rich / graphite cells, water-based electrode process

12 Ah nominal capacity
~190 Wh/kg after cell formation

- Prismatic 90 mm x 140 mm, soft packaging
- Wound cell + internal plastic core for mechanical stability

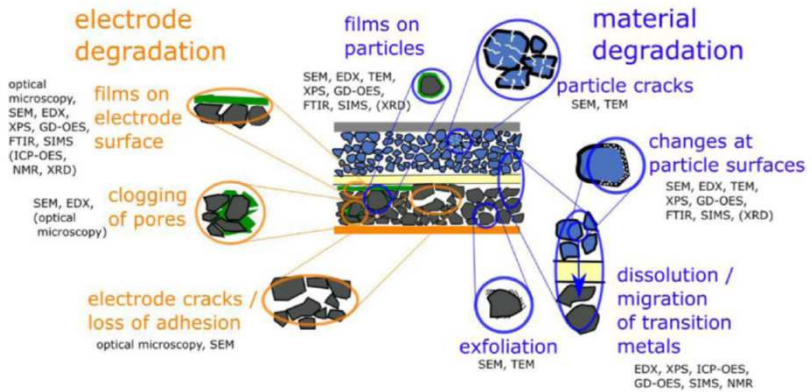




X 10 cells

Tools and methods for ageing evaluation

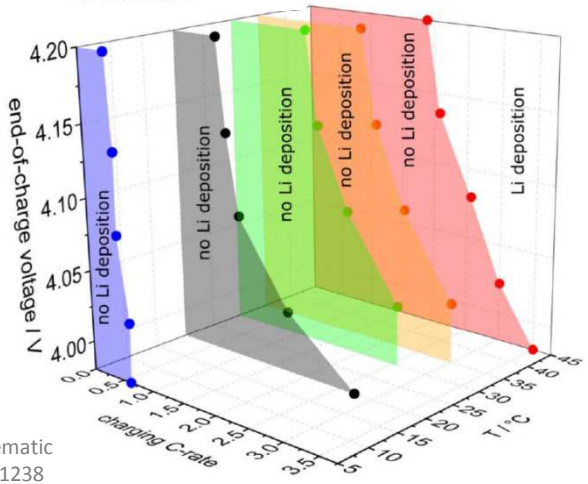
- **Variety of tools** for ageing mechanisms understanding
  - Ante / operando / post-mortem analysis
  - Advanced implementated methods in Mat4Bat: GD-OES spectroscopy, electrochemical analysis, sensors…



T. Waldmann et al., Review—Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis Techniques, *J. Electrochem. Soc.* 163 (2016) A2149–A2164

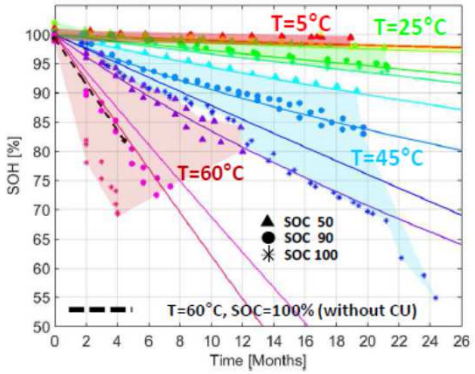
- Main **ageing mechanisms at the anode side**
  - SEI growth
  - Li plating
  - Local Li deposition

Strong interplay of operating conditions [T, C-rate, upper cut-off voltage] to avoid lithium deposition



T. Waldmann et al., Interplay of Operational Parameters on Lithium Deposition in Lithium-Ion Cells: Systematic Measurements with Reconstructed 3-Electrode Pouch Full Cells, *J. Electrochem. Soc.* 163 (2016) A1232–A1238

- **Semi-empirical models of ageing data**
  - Cell resistance evolution
  - Capacity loss



Impacts

- **Commercial exploitation / Technology transfer**
  - Advanced materials & process know-how: PVdF latexes, carbon materials (graphite, addititives), electrolytes, Li-rich material
  - Predictive ageing models → BMS development

→ Identified market: cell manufacturers, modules and packs integrators, OEMs

- **General advancement of knowledge**
  - New methods for material characterization and battery testing
  - Deep understanding and verification of ageing and degradation processes in electrical vehicle batteries
  - Networking with actors of battery field, reinforced expertise

→ Extension to other fields of battery storage is possible
→ Battery second life, implementation at module and pack levels, stationnary storage, other battery technologies (Li-ion and beyond)

- **Europe-based industry benefit**
  - New advanced materials for improved Li-ion cell manufacturing
  - Options for the use of environmentally friendly and sustainable materials

Conclusion and recommendations

- Development of **advanced materials for battery storage** is a long process…
  - Maturation time is needed for **low TRL components**
  - **Li-rich cathode material**: very promising, but short lifetime, fundamental research effort needed
  - **Electrolytes**: to be developed according to clear KPI (final application, T, lifetime, cost…), battery cell design and process to be adjusted

- Materials of interest could only be further developed with **industrial perspective**
  - Collaborative projects, workshops… to **share roadmaps**
  - Strong support of **battery cell manufacturers** is mandatory

- **Modeling and simulation tools** to rapidly bridge the gap between scales
  - **Components**: Materials → Electrodes → Cells → Modules → Packs
  - **Process**: Lab → Pilot → Industrial production

MAT4BAT

Advanced materials for batteries

Thank you for your attention