***M**aterials for **A**geing*
***R**esistant Li-ion High Energy*
***S**torage for the **E**lectric*
***V**ehicle*

MARS-EV Project

Overview

Idoia Urdampilleta *IK4-CIDETEC*

Joint EC & EGVIA workshop for advanced automotive batteries research

Brussels, 12/10/2016

This project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement no 609201

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

General information & Consortium

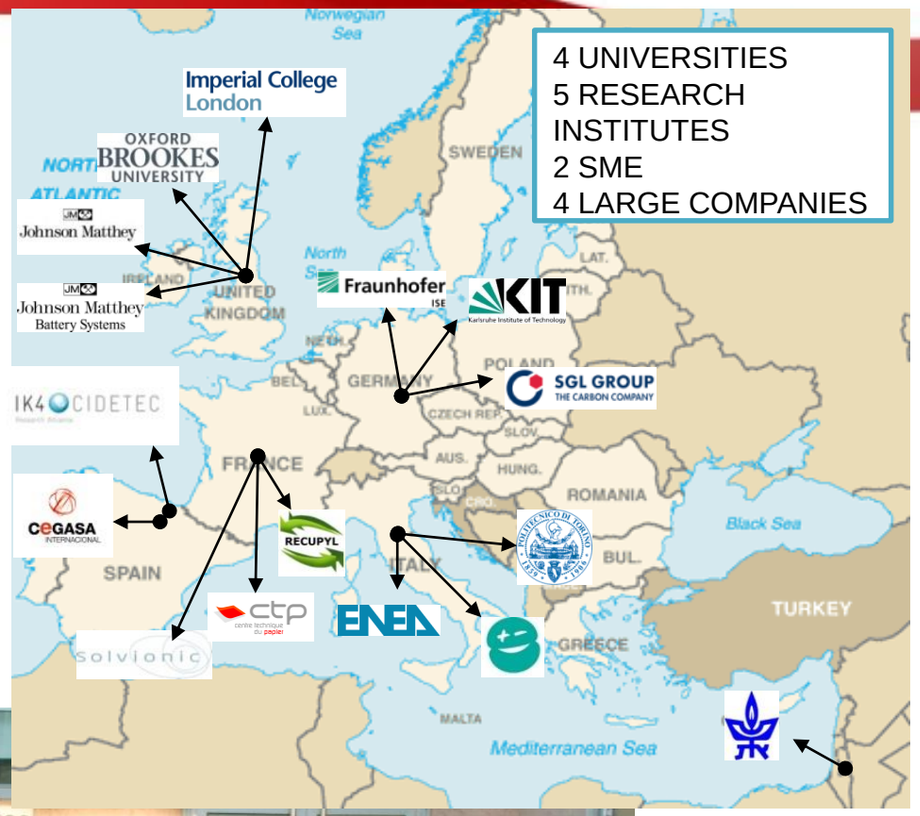
Call: FP7-2013-GC-MATERIALS

Grant Agreement #609201

Topic: **Improved materials for innovative ageing resistant batteries**

- Total budget: 9.0 M€ (EC contribution: 6.6M€)
- Duration: 01/10/2013 – 01/10/2017

16 (now 15) partners from 5 EU member states + Israel



Project Objectives

- Overcoming the ageing phenomenon in **high energy Li-ion** batteries:
  - Development of **materials** through **sustainable scale-up synthesis**:
    - ✓ High energy **electrode materials**: high-capacity anodes and high-voltage cathodes
    - ✓ **Safe electrolyte systems** with improved cycle-life
    - ✓ Industrial scale prototype pouch cell assembly with eco-friendly components
  - **Ageing and life cycle modelling** and assessment:
    - ✓ Modelling of ageing behaviour at electrode and system level
    - ✓ Full life-cycle and recycling assessment

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

MARS-EV

Project Concept: High Energy & Durable Li-ion cell

New high voltage, nanostructured cathodic materials
High capacity Carbon & Si based anode
Polymeric high conductive reinforced electrolyte
Ionic Liquids & high-voltage additives
Ecodesigned cellulose based packaging

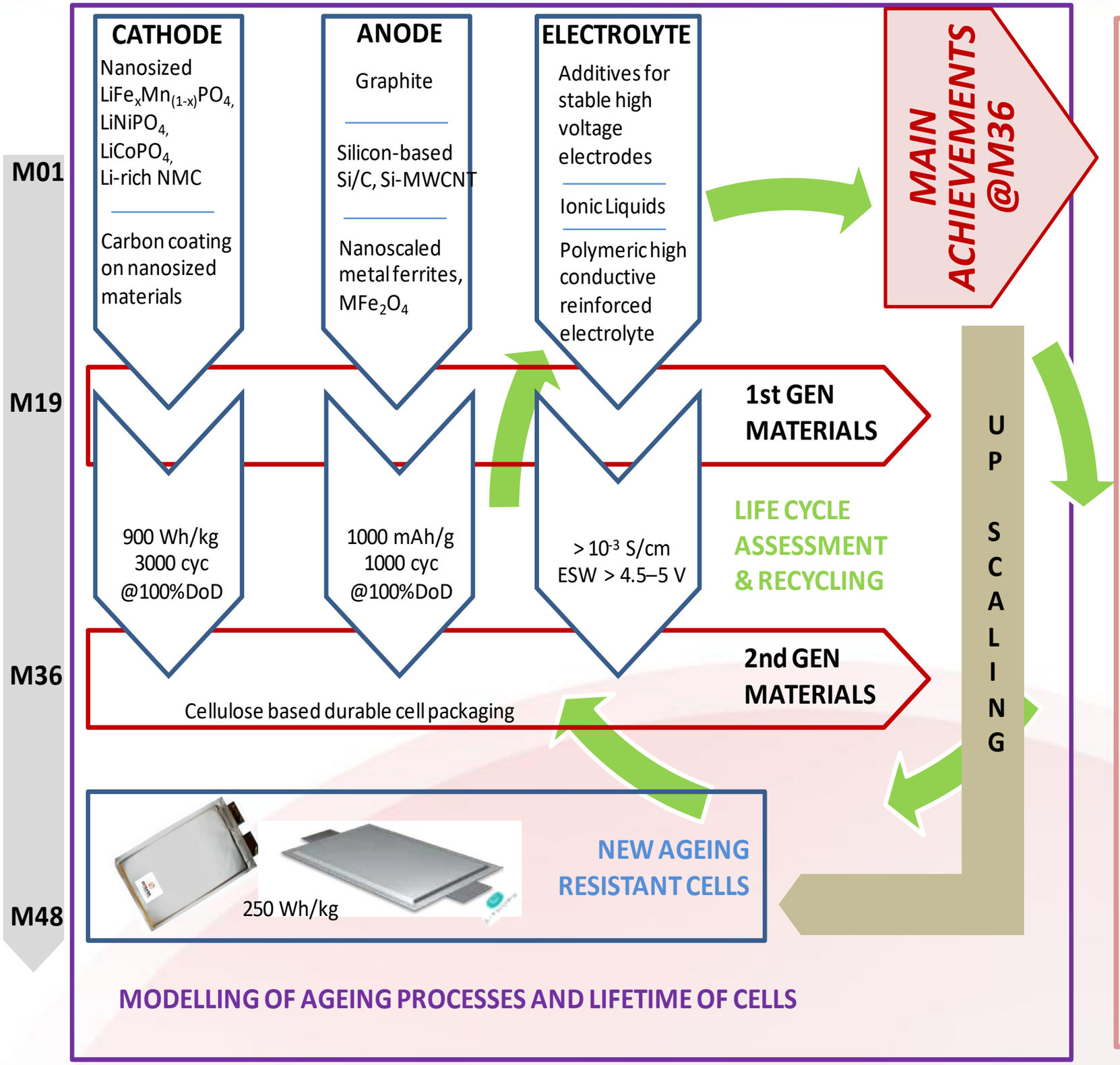
Production of long life cell at lab level (<1000cm²)
Production at the pre-industrial level (B5 format cells)

Cell ageing studies and modelling

Life Cycle Assessment from materials to cell recycle/reuse

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

Project Work Plan Overview and Timeline



Definition of materials & cells production specifications

Materials synthesis at lab-scale *(<10g):* ***Li-rich NMC, $LiCoPO_4$*** *(GEN-1 for scale-up assessment),nano-Si, ZnM_2O_4*

Safe electrolytes: *Ionic Liquids, additives for high-V cathodes, , polymer electrolytes, compatibility with Si anodes*

Scaled-up Graphite *anode (aqueous processing). Scale-up of* ***$LiCoPO_4$/C*** *, optimisation ongoing for cell prototyping*

Cellulose-based pouch *material with barrier properties TBC*

Baseline (NMC & LFP) ageing tests (modelling *ongoing).*

LCA *on baseline completed and assessment on new electrochemistry ongoing*

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

WP3: REQUIREMENTS and SPECIFICATIONS

Requirements for small EV & materials and cell specifications DEFINED @M12

Johnson Matthey
Battery Systems

D3.1 *- Definition of MARS-EV battery pack architecture for small BEV City Car (~Daimler Smart) and translation to cell*

MARS-EV City Car			
Nominal Pack Energy	17.2kWh	Chemistry	HV Cathode / Si
Usable Energy	12kWh	Capacity	20Ah
Series x Parallel	82S x 3P	Type	Pouch
Voltage Range	250-370V	Voltage Range	TBD
Peak Disch. Power	60kW (30sec)	Weight	<300g
Peak Charge Power	40kW	Volume	<120cm^3
Cont Discharge Power	30kW	Energy density	250Wh/kg
Cont Charge Power	20kW (charger)	30s Peak Current	60A
Thermal Management	?	Cont. current	30A

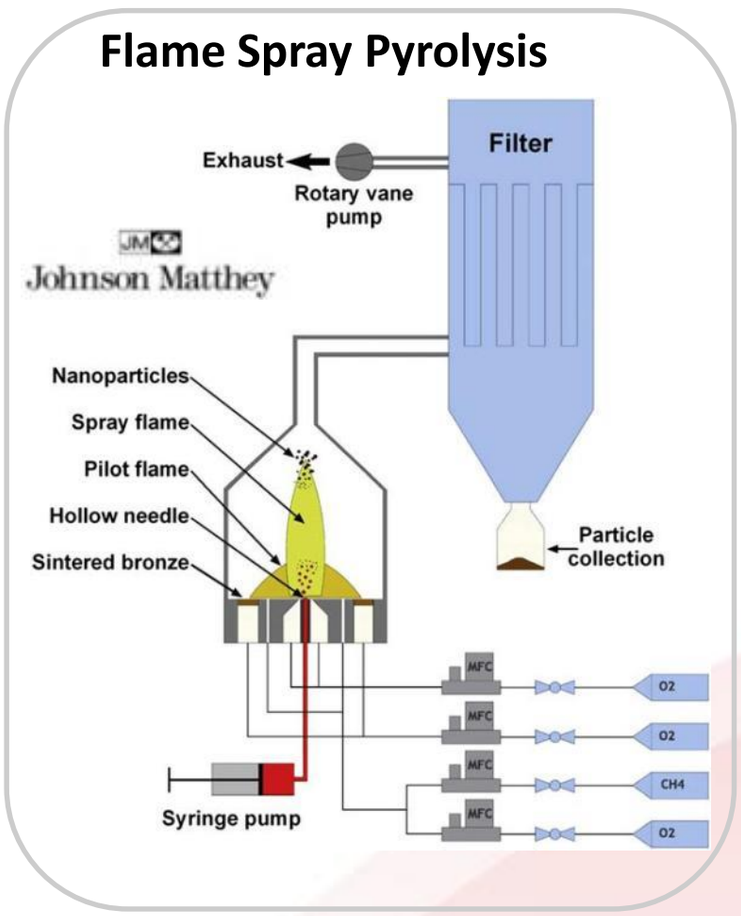
D3.3 *–MARS-EV cell specifications & test protocols*

Parameter	MARS-EV target (D3.1)	CEGASA format	LITHOPS format
Chemistry	HV Cathode / Si		
Voltage range / V	TBD [3.6-4.6]		
Type	Pouch	Pouch, Tabs on same side	Pouch, Tabs on opposite sides
Capacity / Ah	20	15	10
Dimensions: HxW /mm (tabs excl.) Thickness / mm		 263x162 6	 250x164 6
Weight / g	<300	<250	<225
Volume / cm^3	<120	<255	<250
Energy density / Wh/kg	250	<240	<200
Power density / W/kg (10s, 50%SoC)	2000	2000	2000
30s Peak *	3C / 60A	45A / 4C	30A / 6C
Cont. Discharge *	1.5C / 30A	22.5A / 2C	15A / 3C
Cycle life (80% C_{ini})	>3000 cycles @1C/1C; 100% DoD 4000 cycles @1C/1C; 80% DoD		
Operating Temperature	-20ºC to 55ºC		
Safety	EUCAR 3 (No venting, fire or flame; no rupture; no explosion. Weight loss <50% of electrolyte weight)		

** To choose C-rate or Intensity (A) by pack assembler as most representative value*

High Voltage Cathode synthesis developed

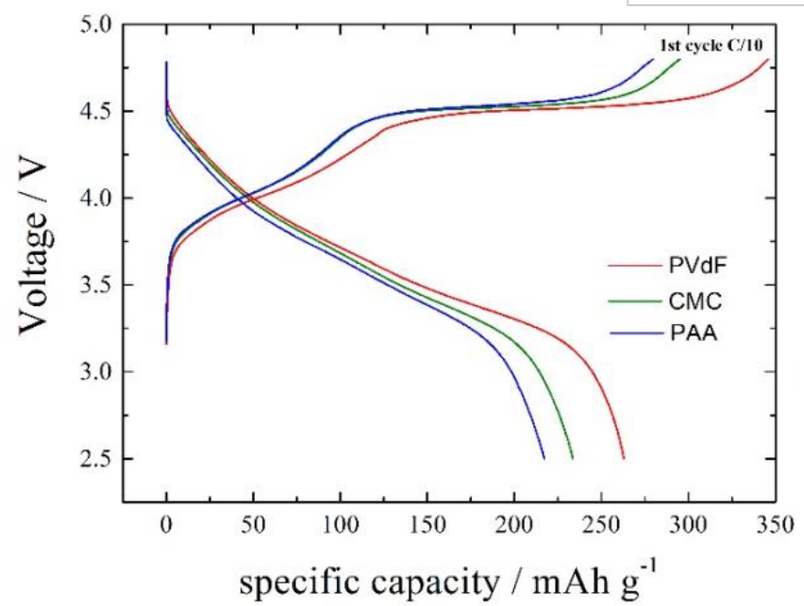
- **Nanodimensional 4.8V $LiCoPO_4$** by Flame Spray Pyrolysis
- **Coated Li-rich NMC** with increased capacity and cycle-life

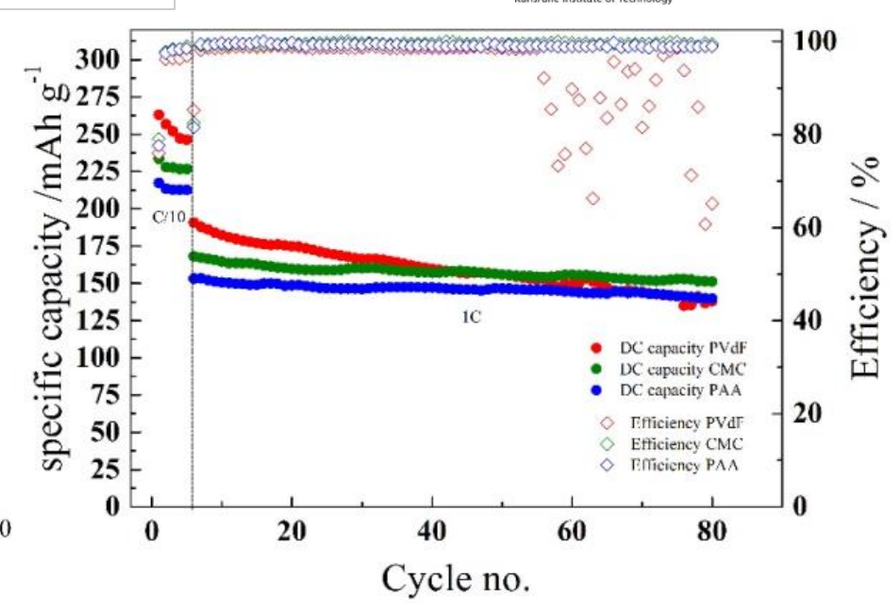


LCP-FSP under patent

MS2 Target: 900 Wh/kg-active material, 3000 cycles

Li-rich NMC





LR-NMC/VO_x coated particles allowing electrode preparation using **waterborne binders** with delayed capacity decay

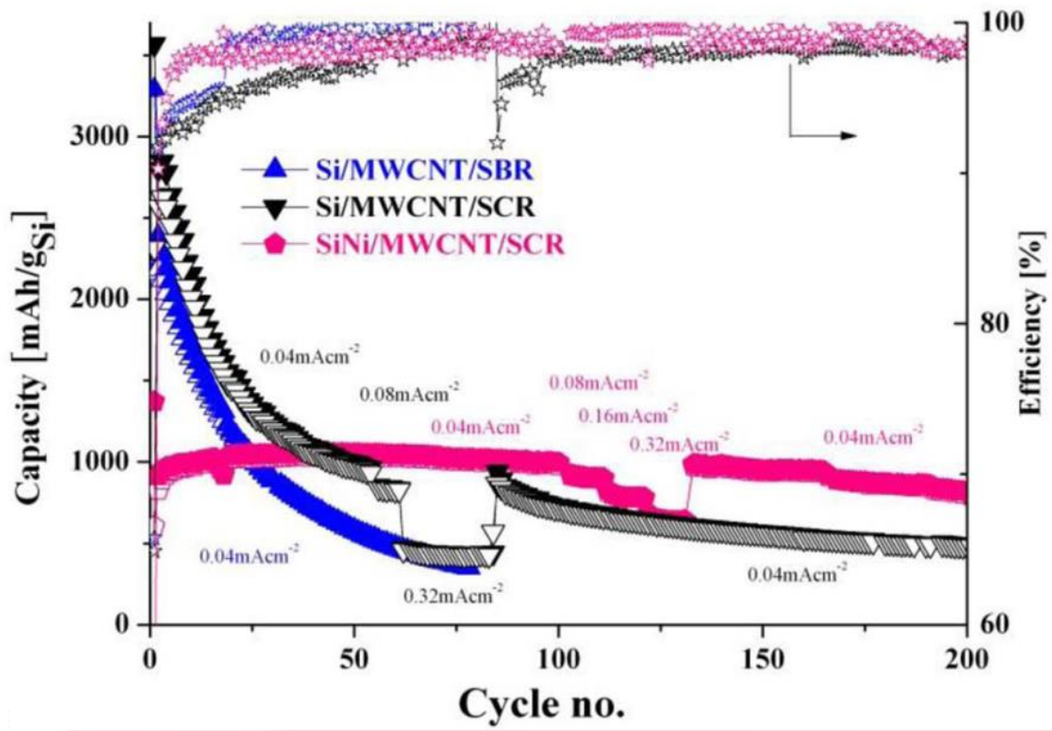
N. Laszczynski et al. ChemElectroChem 2(11) 1768–1773 (2015).
DOI: 10.1002/celc.201500219

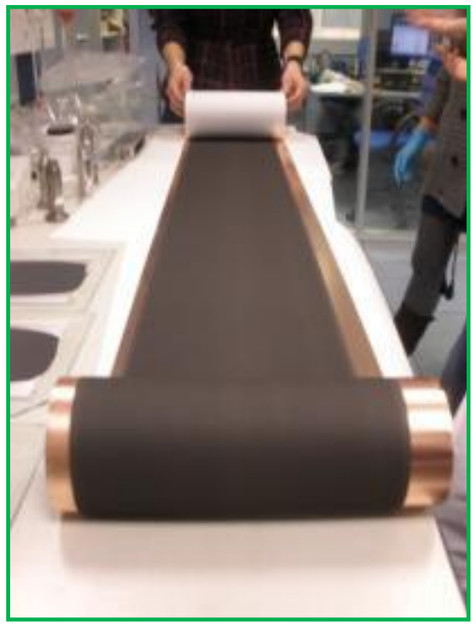
WP5: HIGH CAPACITY ANODES

- Low-cost, high-capacity **nanosized silicon-based and metal ferrite anode materials**
- **Anode protecting coating** for long-cycle-life Li-ion battery
- Investigation of **ageing mechanisms**. Interfacial phenomena and cycle life of cells optimization
- **Scaling-up** of candidate anode materials

MS4 Target:
600 mAh/g,
300 cycles

K. Goldshtein et al., Journal of The Electrochemical Society, 162 (6) A1072-A1079 (2015) DOI: 10.1149/2.1111506jes





MAIN ACHIEVEMENTS @M36

Nano-Si composites with MWCNT - electrolyte compatibility for stable SEI → 600mAh/g, >150 cycles

Synthesis of high capacity $ZnFe_2O_4$ by FSP (lab-scale)

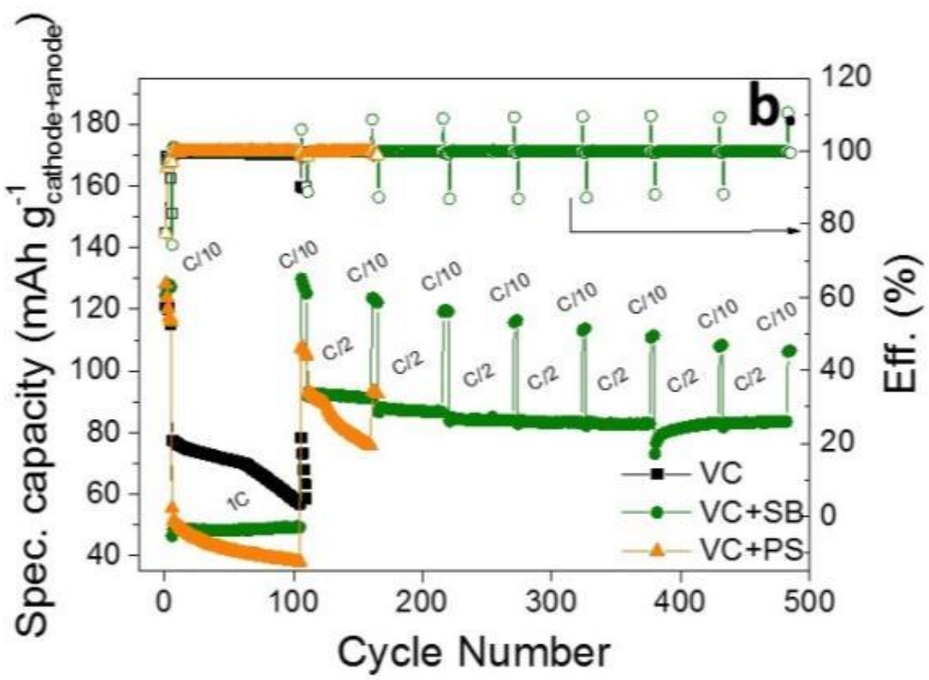
Optimized Graphite for aqueous slurry processing → pilot-line coating

WP6: SAFE ELECTROLYTES

- Electrolyte formulations with selected additives increasing cycle-life of Li-rich NMC cells

SB > PS

85% retention over 485 cycles



Agnese Birrozzi et al. *Beneficial effect of propane sultone and tris(trimethylsilyl) borate as electrolyte additives on the cycling stability of the lithium-rich NMC*, Journal of Power Sources 325, 525–533 (2016).

- Solid polymer electrolytes with no-flammability and performance at 20ºC

- UV-cured = 0.5 mS·cm^{-1} (RT)
- PEO-IL > 1 mS·cm^{-1} (20ºC)

PEO:TEGDME:TFSI

Luca Porcarelli et al. *Super Soft All-Ethylene Oxide Polymer Electrolyte for Safe All-Solid Lithium Batteries*, Scientific Reports 6, Article number: 19892 (2016); doi:10.1038/srep19892

Ionics Liquids: Purification for Pyr-based (FSI, TFSI); testing with LFP, LCP

2 candidate formulations with additive / IL mixture for selection and upscaling

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

WP7: HIGH ENERGY CELL DESIGN & PRODUCTION

Optimise and **scale-up electrode formulation**

Integration of best electrolyte composition into the cell assembly process

Developing **new generation cellulose-based packaging** for Li-ion pouch cells

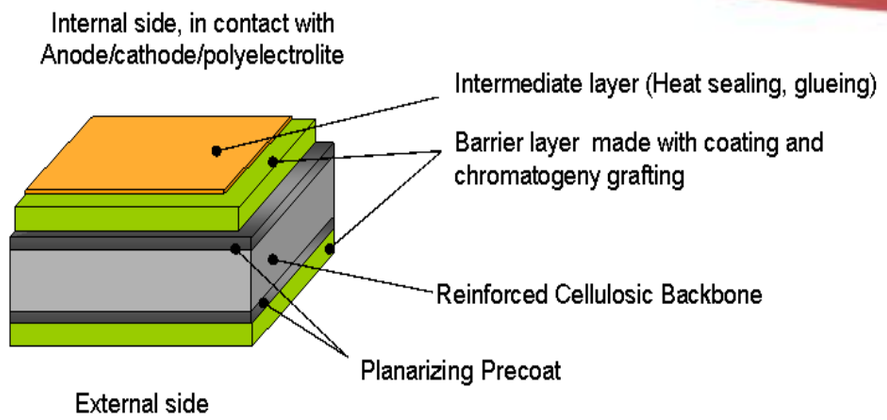
Developing **Li-ion pouch cells** from small (>500cm²; 1Ah) cell up to **automotive size** (20000cm²; >20Ah)

Target: 250 Wh/kg
3000 cycles at 100% DOD

MAIN ACHIEVEMENTS @M36

Technical specifications for new cellulose-based packaging;
2 routes towards achieving barrier properties

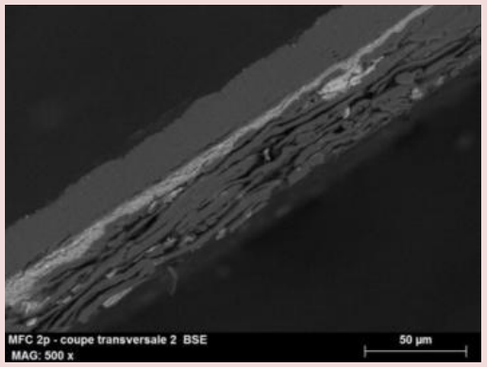
WVTR <0.1g/m²/day (23°C, 85%RH)
OTR <0.1cm³/m²/bar/day (23°C, 0%RH)

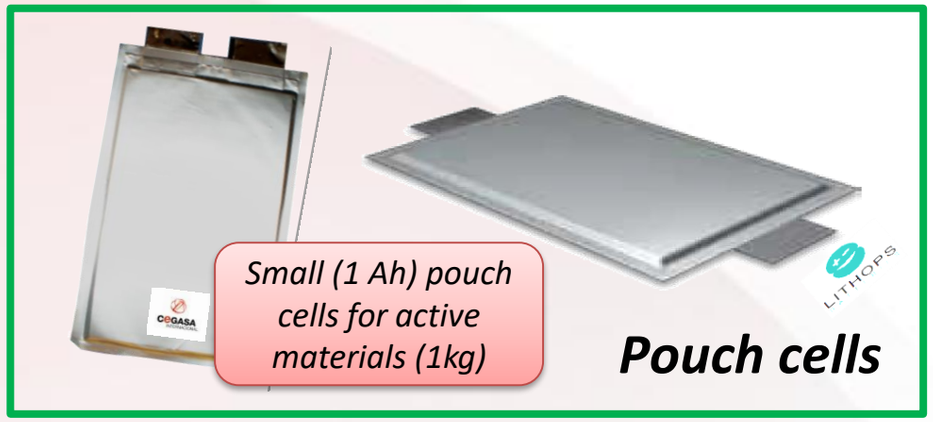


Scheme of the layer assembly for cell packaging

Coated and chromatogeny grafted paper

Ecofriendly & low cost cellulose-based packaging with water vapour barrier





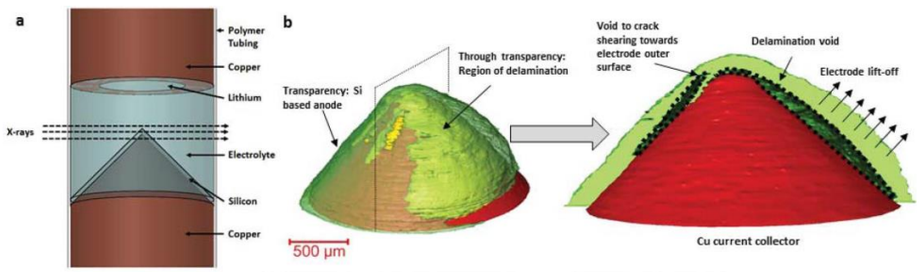
Pouch cells

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

WP8: MODELLING OF CELL AGEING

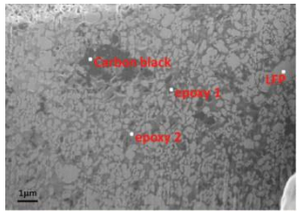
- Electrode-level modelling:
3D Imaging IN-OPERANDO of Si anodes

Imperial College London



F. Tariq et al., ECS Electrochemistry Letters, 3 (7) A76-A78 (2014) DOI: 10.1149/2.0081407eel

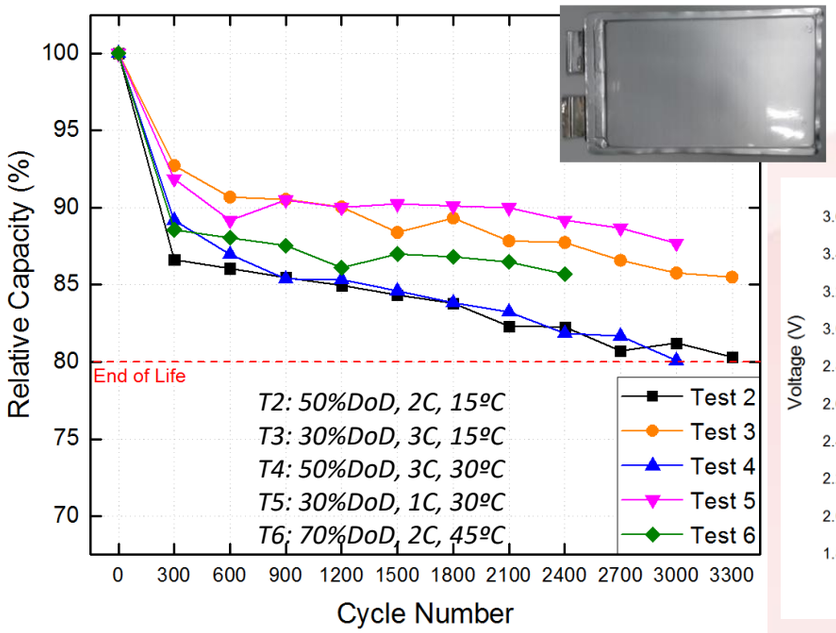
Novel preparation method applied to LFP electrodes (High-Res FIB-SEM)



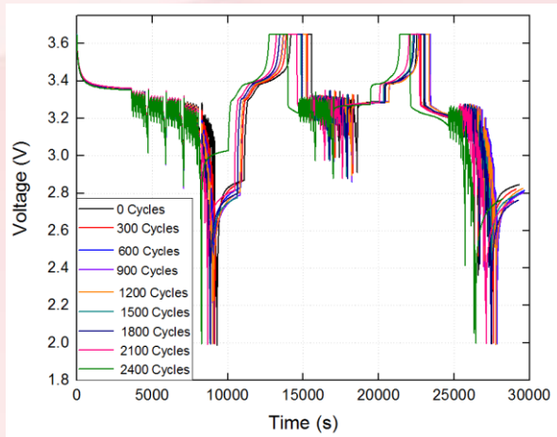
Moshiel Biton et al., J. Electrochem. Soc. 164, (1), A6032-A6038 (2017) DOI: 10.1149/2.0061701jes

- Modelling of baseline C/NMC and C/LFP cells: Design of Experiments (Taguchi) for ageing tests → electrical model (SOC & SOH algorithms - Kalman Filter)

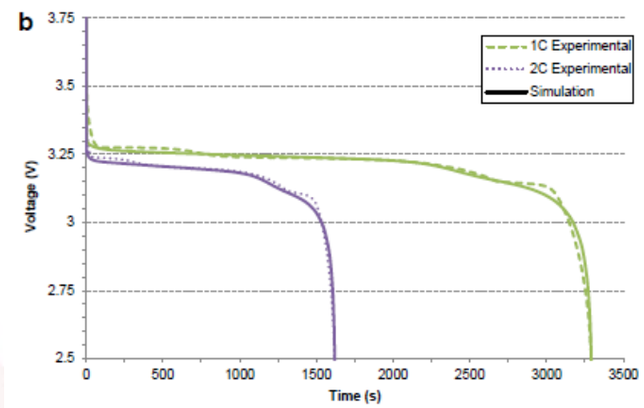
Fraunhofer ISE IK4 CIDETEC JM Johnson Matthey Battery Systems

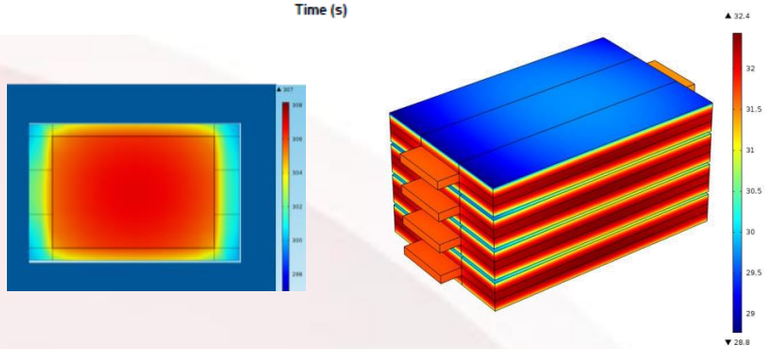


NEDC Profile applied to check SoH estimation under real battery conditions



- LFP pouch cell (P2D + 3D thermal) model developed for battery pack optimisation





Arpit Maheshwari et al, Journal of Power Sources 307 (2016) 160-172 DOI: 10.1016/j.jpowsour.2015.12.111

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

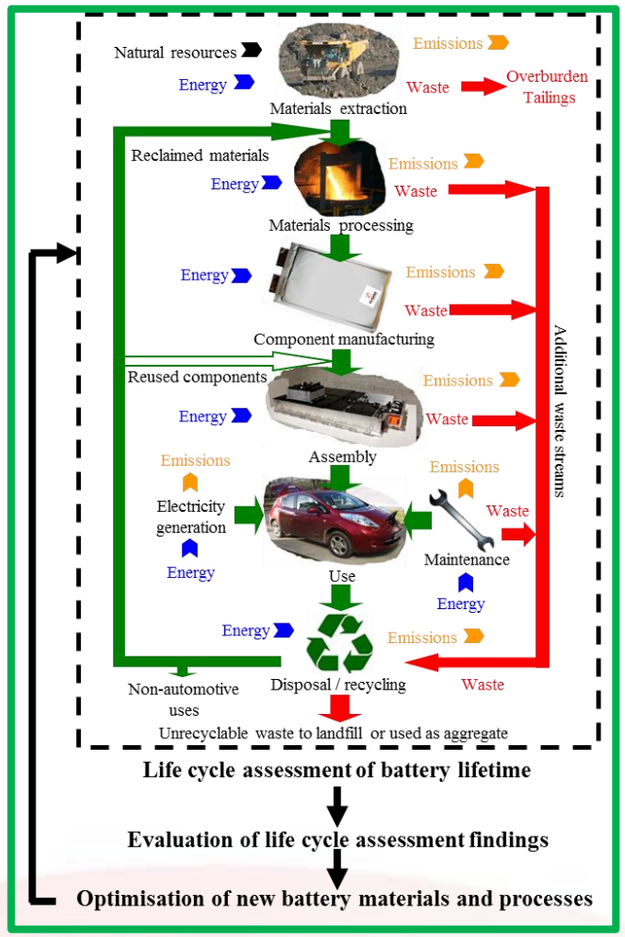
WP9: LCA & RECYCLE/REUSE

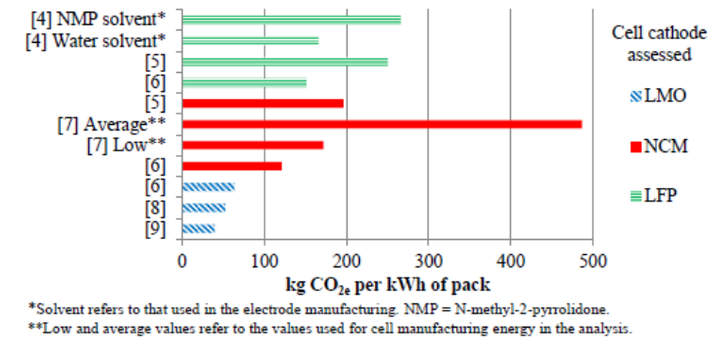
Regulatory assessment on REACH and CLP (GHS) aspects

Technical/economical/environmental optimization of the product through **LCA** (to assess the impact of key environmental parameters) and cost assessment

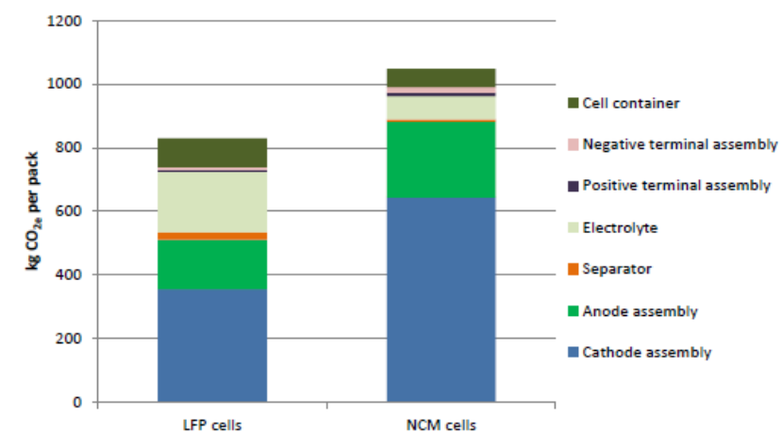
Industrially **optimized cells recycling** process (target of a minimum of **50% recycling rate**)

To evaluate the **reutilization** of different battery components for further uses





*Solvent refers to that used in the electrode manufacturing. NMP = N-methyl-2-pyrrolidone.
**Low and average values refer to the values used for cell manufacturing energy in the analysis.



Cell manufacturing (pilot-scale) energy removed

Lower impact of LFP with aqueous electrode processing

MAIN ACHIEVEMENTS @M36

REACH , CLP) completed for MARS-EV materials: no restrictions –updating for new materials

Initial baseline LCA (NMC and LFP cells) completed

Data gathering for new materials & cells

Assessment of recycling routes for new materials

Materials for Ageing Resistant Li-ion High Energy Storage for the Electric Vehicle

WP10: Training, dissemination and exploitation

Dissemination Materials

Project website www.mars-ev.eu

Threefold Leaflet

On-line Newsletters (every 6 months)

Dissemination and Training activities

12 published scientific articles

> 20 contributions at international conferences and workshops

E-MRS Fall 2016 - Symposium N on *Materials for high energy EV batteries*

Exploitation activities

Plan for Use and Dissemination of Knowledge DRAFTED:

21 Exploitable Results identified and characterised for monitoring and update

(Patent application on high-V active material)

Conclusions – Summary of results

- High Energy electrode active materials synthesised and optimised at lab scale:
  - Cathodes: Li-rich NMC by co-precipitation; $LiCoPO_4$ by FSP *+ coating*
  - Anodes: nano-Si/MWCNT composites, Artificial-SEI formation; ZnM_2O_4 by FSP
- Materials synthesis scale-up: modified graphite (>10kg) and LCP-FSP (1kg)
  - Pouch cell prototypes to be assembled & tested in the final year of the project
- Greener electrode manufacturing using waterborne binders (aqueous slurry): Modified Graphite/CMC/SBR anodes & LR-NMC with CMC, PAA
- Green & safe electrolyte development:
  - Conventional + IL mixtures; additives (TSB) for high-V, compatibility with graphite & Si anodes
  - Solid Polymer electrolytes: UV-cured, IL-containing [> 1 $mS \cdot cm^{-1}$ (20ºC)]
- Ecofriendly cellulose-based pouch packaging with water moisture barrier
- 3D Imaging (in-situ and/or high-res) of electrodes
- Electrical and thermal models for ageing of baseline (NMC & LFP) cells
- LCA on baseline completed and assessment on new chemistry ongoing

@MARS_EV_FP7

Thanks for your attention!

More information at **www.mars-ev.eu**

Further thanks to all MARS-EV partners!!

iurdampilleta@cidetec.es

IK4 CIDETEC
Research Alliance