Project summary

Li-ion batteries today exceed by a factor of 2.5 any competing technology thanks to their energy density. Although already in the market place, progress is still required to meet the stringent requirements of the electric transportation market: e.g. increase of energy density and significant enhancement of service life on both cell level (standardization of cell design, cell chemistry, material costs) and battery level (module design, battery management system with active cell balancing, packaging, thermal management system) thanks to innovative materials and technologies and optimization of process characteristic.

Research and development activities within MARS-EV project aim to overcome the ageing phenomenon in Li-ion cells by focusing on the **development of new electrochemistries**: high-energy electrode materials (250 Wh/kg at cell level) via sustainable scaled-up synthesis and safe electrolyte systems with improved cycle life (> 3000 cycles at 100%DOD). Through industrial prototype cell assembly and testing coupled with modelling, the understanding of the ageing behaviour at the electrode and system levels will be improved. Finally, it will address a full life cycle assessment of the developed technology.

The MARS-EV project has **six main objectives:**

1. synthesis of novel nano-structured, high voltage cathodes (Mn, Co and Ni phosphates and low-cobalt, Li-rich NMC) and high capacity anodes (Silicon alloys and interconversion oxides);
2. development of green and safe, electrolyte chemistries, including ionic liquids, with high performance even at ambient and sub-ambient temperature, as well as electrolyte additives for safe high voltage cathode operation;
3. investigation of the peculiar electrolyte properties and their interactions with anode and cathode materials;
4. understanding the ageing and degradation processes with the support of modelling, in order to improve the electrode and electrolyte properties and, thus, their reciprocal interactions and their effects on battery lifetime;
5. realization of up to B5 format pre-industrial pouch cells with optimized electrode and electrolyte components and eco-designed durable packaging; and
6. boost EU cell and battery manufacturers via the development of economic viable and technologically feasible advanced materials and processes, realization of high-energy, ageing-resistant, easily recyclable cells.

The project concept is thus translated to the following activities and targets:

Electrode materials will be synthesized at lab-scale: nanosized $LiFe_xMn_{(1-x)}PO_4$, $LiNiPO_4$, $LiCoPO_4$ and Li-rich NMC systems with low cobalt content will be synthesized choosing the most suitable synthesis route to obtain nanostructured composite particles targeting 900Wh/kg and 3000 cycles at 100%DoD. On the other side, besides the use of graphite as anodic material, new Si/C based, spinel ferrites and Li metal anodes will be considered to achieve 1000 mAh/g stable capacity over 1000 cycles. Best performing materials will be scaled-up in two generations.

The interface electrode/electrolyte is one of the most critical points to achieve high density, good cyclability and power rate. Moreover the use of polymer electrolytes is mandatory for Li-ion cell safety. Membranes with high mechanical properties, ecofriendly and reinforced, UV and/or thermally cured and based on epoxy resins will be considered.

Li-ion cells from the lab-scale (<1000 cm^2) to the preindustrial scale (up to 20000 cm^2, B5 format) will be realized as proof of concept and tested on electrochemical performance, lifetime and safety.

The choice of materials, synthesis methods and the cell assembly processes will be driven by the Life Cycle Assessment that will be realized taking into account the recyclability of the complete cells (>50% recycling rate). Modelling at the materials level (electrode/electrolyte interface) as well as the system level (cell ageing, SOH at different regimes) will also guide the materials and cell development and testing.

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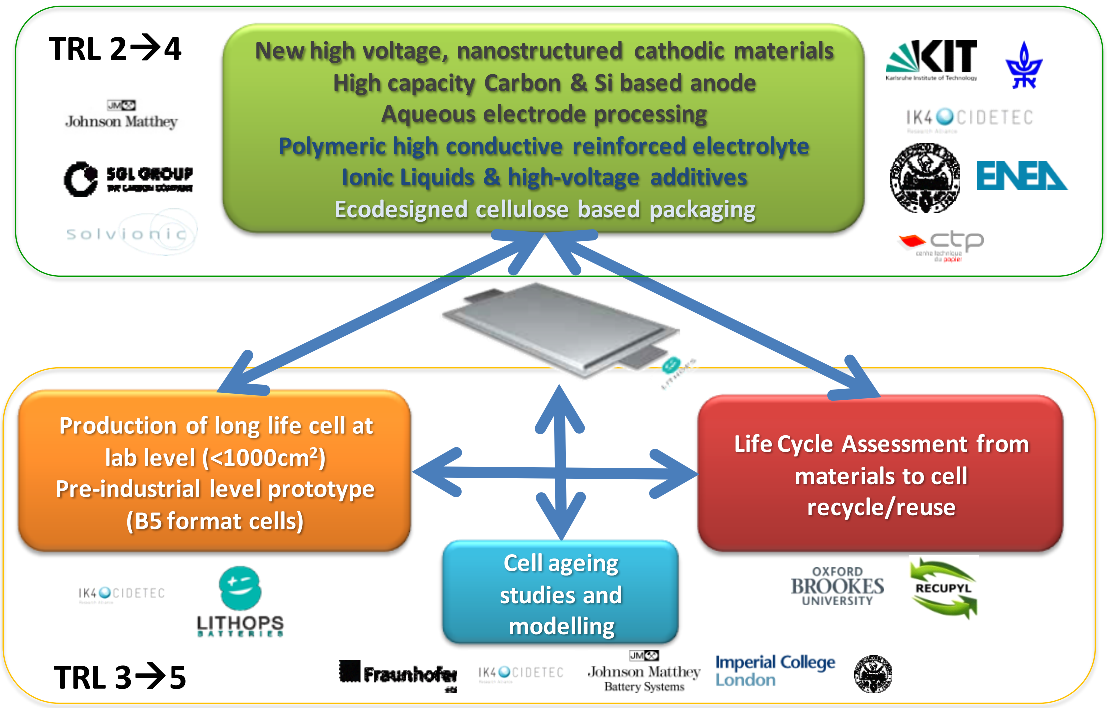
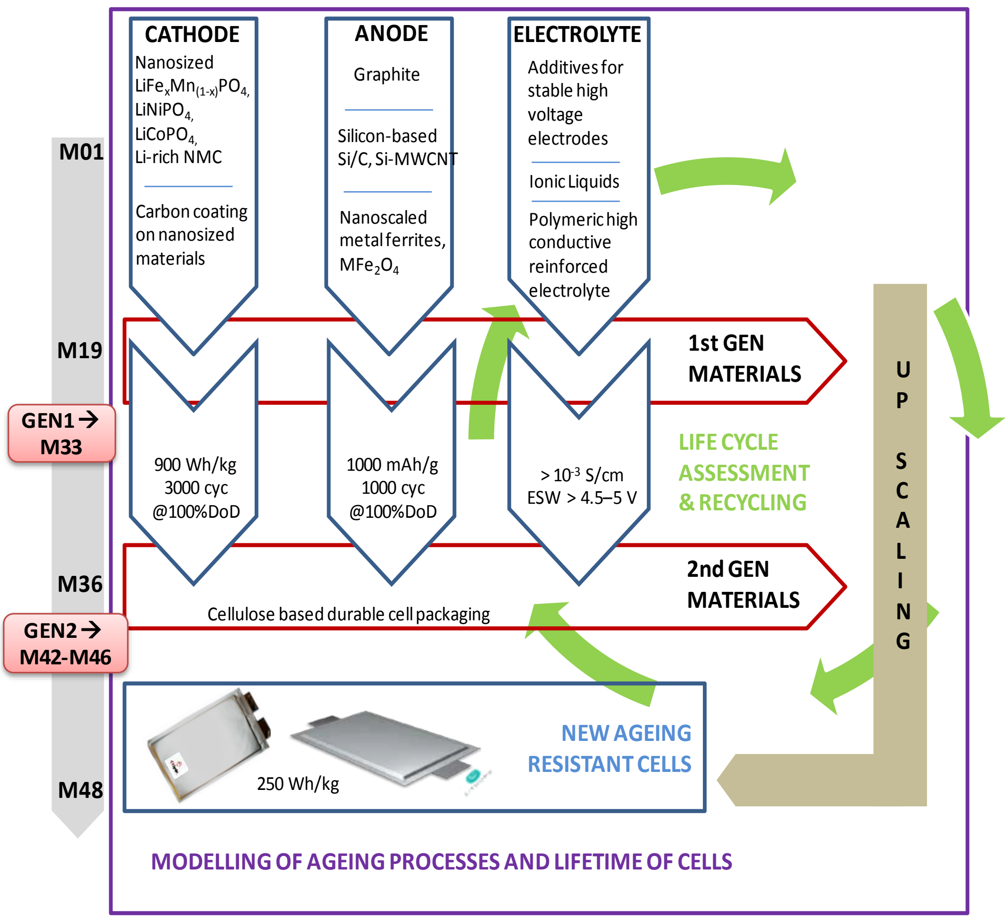


During the first 18 months, efforts were focused on the **development at lab-scale** of high energy cathode and anode materials through new -potentially low cost and environmentally friendly- synthesis methods, as well as safer electrolytes through solid polymers and ionic liquids. With the progress achieved, a selection of coated cathode active materials, silicon composite and UV-cured polymer electrolyte were candidates to be upscaled in the following period. Water based slurry formulations to manufacture the electrodes were developed. **Ageing tests and modelling started** based on commercial cells chosen as baseline chemistries (C/LFP and C/NMC) for the new materials in the project. **Regulatory assessment** of the new proposed materials **and baseline LCA were accomplished** to analyse the eco-compatibility of the MARS-EV materials and cells.

During the second reporting period (M19-M36), efforts **focused on the scale-up** of selected coated cathode material, available optimized graphite for water-based anode manufacturing and suitable high-voltage electrolyte for the **first generation of cells**. Further development of possible 2nd generation materials of high energy cathode and anode materials through new -potentially low cost and environmentally friendly- synthesis methods, as well as safer electrolytes through solid polymers and ionic liquids, has continued at lab-scale. **Ageing tests and modelling on commercial cells** chosen as baseline chemistries (C/LFP and C/NMC) are nearly finished and **electrical and thermal models (SOC, SOH algorithms) have been developed**. **Referenced LCA** to analyse the eco-compatibility of the **MARS-EV materials and cells has been launched** after the GEN1 components selection, as well as the hydrometallurgical recycling route analysis achieving more than 50% recycling rate and closed-loop materials recovery.



During the last year (M37-M48), efforts have been invested on the scaled-up **manufacturing of electrodes** (high-voltage cathode and optimized graphite anode) and

assembly of prototype cells, both **10Ah** B5-sized **GEN1** (MEG-1/LFP both water-based) and small **1Ah GEN2 cells** with high voltage cathodes (water-processed LNMO and organic LCP/C) and improved MEG2 graphite. Extensive study has also been needed to find a **suitable electrolyte for high voltage** operation with LCP cathode for these cells. Although limited by time, the cells have been tested. Cellulose-based packaging "Structure 2" has proven targeted barrier properties to be used as lighter and ecofriendly pouch material for cells. Further development of Silicon-based anodes as well as safer electrolytes through solid polymers and their compatibility with new cathodes has continued at lab-scale. Ageing tests and modelling on baseline commercial cells (C/LFP and C/NMC) were finished and **electrical and thermal models (SOC, SOH algorithms) have been developed**. The LCA on the MARS-EV Gen2 (LCP cathode; aqueous electrode manufacturing, new packaging) has been completed, as well as an hydrometallurgical recycling route achieving **more than 75% recycling** rate and closed-loop materials recovery.

Main project achievements:

- Definition of MARS-EV battery pack architecture for small BEV City Car (~Daimler Smart) and translation to cell and materials specification and selection criteria.
- Synthesis of novel nano-structured high energy active materials at lab-scale:
    - Low temperature synthesis of $LiMPO_4$ (M=Fe, Mn) using Ionic Liquids has been studied. A method to recover and purify the ionic liquid utilised as reaction medium was developed using NaOH, in order to make possible the recycling for further syntheses.
    - $Li_2Mn_3Si_4O_{12}$/C nanocomposite preparation providing more than 200 mAh/g at C/20 but low cycle-life.
    - **High voltage cathodes:** C-coated $LiCoPO_4$ (LCP/C) by Flame Spray Pyrolisis (FSP) and VOx-coated Li-rich NMC with increased capacity and cycle life (~850 Wh/kg-active)
        - **C-$LiCoPO_4$ by FSP has been produced at 1kg-scale** (**GEN2 upscaling**) and delivered for electrode manufacturing.
    - **High capacity anodes**: **Ni-doped Silicon MWCNT** with compatible electrolyte, achieving 600 mAh/g for more than 400 cycles; new approach for ART-SEI formation by Si ball milling with LiF providing 2500-2000 mAh/g-Si for >110 cycles. Improvement of the formulation and procedure of anode preparation by replacement of 10%MWCNTs by 0.5%SWCNTs and knife milling instead of high-energy ball milling method.
        - **Si:Ni [1:0.075] with 0.5%SWCNTs and knife milling** exhibit over **1000mAh/gr_{anode}, for 250 of cycles**.
    - **MEG-2 optimised graphite** has been developed providing 350mAh/g at >1C in technical electrodes, to be used in GEN2 cells and also benchmarked in another EU H2020 project.

- Electrode preparation using aqueous binders: Li-rich NMC with CMC and Na-alginate has been proven, as well as for high-voltage LNMO commercial spinel (in absence of available LCP); Silicon anode can be prepared with aqueous binders (Li-PAA). **Manufacturing in coating line** for pouch cell assembly:
    - **GEN1 anode with surface modified graphite MEG-1**.
    - High-voltage **LNMO** commercial spinel for small GEN2 cells.
    - LCP cathode formulation with waterborne binders was developed but could not be upscaled. Electrode with PVdF/NMP formulation was produced instead.
    - **GEN2 anode with surface modified graphite MEG-2** has been manufactured.
- Development of green and safe, electrolyte chemistries with high performance even at ambient and sub-ambient temperature for MARS-EV electrode chemistries:
    - **Additives** for high-V cathodes (Li-rich NMC): VC+SB combination delivered capacity of 440 Wh·kg^{-1} (cathode+anode) or 815 Wh kg^{-1} (cathode): 1M $LiPF_6$ in EC:DMC (1:1 w/w) + (2%VC+4%SB) **upscaled to 1L** (GEN1).
    - Additive screening for LCP cathode operation (up to 4.95V): TTSPi and TFEC provide enhanced cycling stabilities and coulombic efficiencies in LCP/graphite full cells. 1M $LiPF_6$ in EC:DMC (1:1 w/w) + 2%TTSPi **upscaled to 200mL** (GEN2).
    - High purity (through lower cost purification route) pyrrolidinium-based ILs (TFSI and FSI): LiTFSI-PYR_{13}TFSI-EC/DMC has shown the highest conduction values whereas the additive-free LiTFSI-PYR_{13}FSI-EMIFSI sample behaves as well as the mixed IL/organic electrolytes. At room temperature, conductivity values of 10^{-2} S cm^{-1} are approached. Not compatible with LCP.
    - Non-flammable **Solid Polymer Electrolytes** (UV-cured) showing conductivities of 0.5 mS·cm^{-1} (RT), wide ESW and mechanical integrity. Long-term performance in both Li-metal and Li-ion cells and cycling at high-V (LNMO).
- Development of eco-designed **cellulose-based durable cell packaging**: water vapour and oxygen transference barrier properties achieved. N**ew generation of paper based barrier product suitable for housing Li cells**. [PVdC/M2/MFCPVdC], thickness ~96µm; ~125g/m^2. **Weight reduction of -69%** vs. standard ALF pouch material.
- **Manufacturing of GEN1 10Ah cells** with 1st selected materials: MEG-1 96% aqueous anode and conventional LFP-PVdF cathode.
- **Manufacturing and testing of GEN1 10Ah cells** with water-based electrodes: MEG-2 94% aqueous anode and LFP cathode.

- **Manufacturing and testing of GEN2 1Ah cells with waterborne LNMO/MEG2 and NMP-based LCP/MEG2:** LNMO cells (4.7V) with stable cycling for >250 cycles.
- Development of a cell model including electrical, thermal and ageing characteristics:
  - **Design of Experiment for ageing tests** of baseline C/NMC and C/LFP commercial cells. Test protocols and test matrix were developed. Baseline 2.15Ah 18650 C/NMC completed and 15Ah pouch C/LFP cells still ongoing (>4000cycles).
  - Cycling and calendar models are developed in accordance to the ageing test: **Model checked with aged batteries (SoH down to 90%)** with 0.6% average absolute error under NEDC profile for both cells chemistries. SoH estimation completed.
  - Modelling of the thermal behaviour on cell and pack level has been carried out employing a multi-physics (electrochemical, thermal, fluid-dynamic) and multi-scale approach (Unit-cell, Pouch cell, Module and Pack).
  - Electro-thermal model completed and used for **life-time optimization and battery pack control**: 1st and 2nd order equivalent circuit model was parameterized and validated for NMC cells, with good accuracy for the prediction of the temperature. Life-time model provided enhancement of more than 100% when operating the cells at 45°C.
  - 3D Imaging (tomography) supported modeling: **IN-OPERANDO** has been realized for **Silicon** anodes. **3D reconstructing commercial battery electrodes (LFP cathode,** Gen0 & Gen1 cells**)** utilizing newly developed contrast enhancing epoxies A **new approach** for mechanical testing to **measure the mechanical properties of electrochemically deposited dendrites** in Zn-air, applicable to Li anode.
- Environmental assessment of the product through LCA and development of optimized cells recycling process (target of a minimum of 50% recycling rate).
  - Regulatory assessment on **REACH and CLP (GHS)** aspects completed for MARS-EV materials: **no restrictions** were found
  - **Baseline LCA** (commercial NMC and LFP cells) completed, showing lower impact for LFP cells produced by aqueous electrode processing. Continually updated and refined as more primary data is obtained (mass production vs. pilot-scale)
  - **LCA of new "Gen2" cell**, LCP/Graphite chemistry and cellulose based packaging: environmental impact consistent, and in some cases lower, than commercial cells.
  - Recycling assessment: **use of a hydrometallurgical route improves the efficiency of cell recycling to 76% and allows a closed loop system to obtain precursor material for electrodes**. **Recycled graphite** from the cells has shown 300mAh/g.