SUPERLION passed through an initial "academic" phase (months 1-18), dominated by basic research efforts by the University partners. This set the scene for the active participation of industrial partners (in WP6: *Device Characterisation and Packaging*) during the second half of the project, aimed at providing essentially a "proof-of-concept" through the fabrication of one or more functioning three-dimensional 3D-MBs. These activities are therefore the prime focus of this *Second Periodic Report*; but first a brief summary of the more relevant results to emerge from the earlier part of the project:

- In the absence of dramatic design breakthroughs during *Period 1*, no important modifications were made to the earlier defined geometrical and materials limitations: Area Gain (A.G.) factor 30; benchmark "footprint" capacity: 30-50 μAh/mm^2 - delivering an energy density of 100-200 μWh/mm^2 for a stack-thickness of 500-1000 μm.
- Dynamic FEA modelling subsequently exposed significant non-uniformities in current distributions within working cells, which were strongly dependent both on design architecture and choice of component materials. Concretely, this means that synthetic effort to achieve extreme 3D geometries is wasted in terms of improved footprint capacity, if proper attention is not paid to these critical design issues. This has not been fully appreciated - or so clearly demonstrated - earlier.
- Efforts to deposit negative and positive electrode materials as conformal films on nano-structured current collectors gave some new advances: a spin-coating technique was exploited to deposit layers of $LiFePO_4$ onto the surface of reticulated vitreous carbon; a new "copper-trench" current-collector architecture was developed; finally, thin-film solid or polymer electrolytes (conformal films on nano-structured active electrodes or membranes separating the electrodes) have been further developed - especially, the self-assembly of surfactant oligomers on $LiFePO_4$ particles.
- Negative *Sb* and *Cu_2Sb* electrodes have been electrodeposited successfully onto 15μm Cu micro-trenches. Likewise, *$LiFePO_4$* and *$LiCoO_2$* positive electrodes have been deposited onto columnar and needle-like Al current-collectors, and gave good capacity retention at 1C rate. *CuS* cathodes (with a perforated Si substrate) have cycled more than 400 reversible cycles with ~0.1%/cycle capacity-loss for current densities in the range 0.1-2.0 mA/cm^2; the pulse-power capability was most satisfactory, *e.g.*, ~ 160 mW/cm^2 was obtained for discharge pulse-steps of 100 ms. Corresponding *$LiFePO_4$*-cathode cells gave a capacity of 80 μAh/cm^2 with an average potential of 3.4 V after 20 cycles, and a pulse-power peak of ~ 175 mW/cm^2 for a 1s discharge pulse-step. Similar 3D-MB half-cells have been made with carbon foam current-collectors coated with active *MnO_2* and *$LiFePO_4$* cathode materials. The *MnO_2* cells showed capacities per footprint area (mAh/cm^2) up to 200 times greater than for comparable 2D planar electrodes. Charge/discharge behaviour for *$LiFePO_4$* shows a significant increase in capacity in going from using 5 (130 μAh/cm^2) to 10 (870 μAh/cm^2) wt.% inks. The 5% foam gave a >70 % DoD at 14.3 C (charge- and discharge-time: 4 min.), while 10 % foams gave a >65 % DoD at 4.5 C (charge- and discharge-time: 12 min.).
- Two methods for *assembling* interdigitated "trench-type" 3D-MB cells have been developed: dropwise insertion of $LiCO_2$ into the trenches, and attachment of the composite cathode to the anode/polymer structure through the application of gentle pressure. $LiFePO_4$-based 3D-MB half-cells have been assembled successfully with *aperiodic architecture* to give a capacity of 1.5mAh/cm^2. Complete <TiO_2/solid polymer electrolyte/$LiFePO_4$> 3D-MB cells with aperiodic architecture gave a stable OCV, while

concentric Li/$LiFePO_4$ half-cells gave a capacity of 1.5-2.5 mAh/cm^2 for >100 cycles and >200mW/cm^2 pulse-power capability.

Work undertaken by the industrial partners to achieve *proof-of-concept* for 3D-MBs as realistic power sources in micro-devices has focussed on three different test-cell vehicles: an $LiFePO_4$-based flexible flat cell (for thin cells with large footprint-to-height ratio); MC 614 and V500 coin-cells (for foam-based electrodes with larger sample height). To summarize the findings of this work: although 3D-MB test-cells showed promising characteristics in terms of small size and high energy-density per footprint area, their electrochemical performance, including overall cycling stability, must be further improved in certain respects if they are to be used as realistic power sources in future MEMS or medical devices. Generally speaking, these improvements must be made primarily in the materials processing phase; battery production processes must also be optimized, since the intrinsic performance of single-cell components has been well demonstrated on a laboratory scale. Rate capability and pulse performance at a given capacity can also be important factors in some applications; these must also be improved. Finally, internal cell resistance - as reflected by large over-potentials during charge/discharge - should be further reduced. Although very high capacities per footprint area have been demonstrated as a result of the 3D architecture of the electrodes, higher system capacities will also be necessary for some applications, in order to increase their capacity range from µAh to mAh. A higher volumetric energy density will also be required in some applications, especially when higher capacities are needed as the cells get larger. It is relevant to remark that the performance of electrode systems has improved greatly during the course of this project. However, only samples made somewhat earlier in the project could be fully tested by the industrial partners, due to the amount of time needed for a full industrial evaluation demonstrator cells.

The feasibility of incorporating 3D-MB concepts into conventional Li-ion battery production has also been seen an extra bonus of the project. The most interesting candidate was adjudged to be the “aperiodic sponge” architecture, where the solid network of the “sponge” serves as the substrate and electronic conductor for lithium intercalating anode and cathode materials. The sponge or foam material could, in principle, be adopted in a roll-to-roll coating process. Metallic Ni-foam is seen as the most suitable for testing the feasibility of this process due to its superior mechanical properties. However, the translation of this 3D-MB cell-design into a production process was severely hampered by the electrochemical stability limits of the Ni-foams. Side reactions (corrosion) at the positive electrode occurred at higher potentials during charging, which led to cell breakdown. Clearly, other materials or material combinations will be needed to get this system to work electrochemically, for subsequent implementation in production technology. Financial aspects must also be carefully evaluated.

By the end of the project, *proof-of-concept* for 3D-MBs has been achieved at a design level, but no pilot-line production of 3D-structured electrode materials or cells is yet in existence.